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DECEMBER, 1928

Absolute X-Ray Wave-Length Measurements — A. P. R. WADLUND 841

A New High Potential X-Ray Tube — C. C. LAURITSEN AND R. D. BENNETT 850

Nuclear Motions Associated with Electron Transitions in Diatomic Molecules — EDWARD U. CONDON 858

New Features of the Red Band System of Sodium — F. W. LOOMIS AND S. W. NILE, JR. 873

Interpretation of the Atmospheric Absorption Bands of Oxygen — ROBERT S. MULLIKEN 880

Infra-Red Absorption Spectra of the Methyl Halides — WILLARD H. BENNETT AND CHARLES F. MEYER 888

Visible Absorption Bands of Colorless Liquids and their Relation to Infra-Red Bands — JOSEPH W. ELLIS 906

Intensity Measurements in the Helium Spectrum — CLARENCE HODGES AND W. C. MICHELS 913

Spectral Excitation by Recombination in the Electric Arc — JANE M. DEWEY 918

Secondary Electron Emission Produced by Positive Cesium Ions — J. M. HYATT 932

Secondary Electron Emission from Molybdenum — J. M. HYATT AND H. A. SMITH 939

Ionization of Carbon Monoxide by Controlled Electron Impact, Interpreted by the Mass Spectrograph — T. R. HOGNESS AND R. W. HARKNESS 936

Ionization Processes in Methane Interpreted by the Mass Spectrograph — T. R. HOGNESS AND H. M. EVALENES 942

Ionic Oscillations in the Glow Discharge — L. A. FARDUE AND J. S. WEBB 946

Critical Photoelectric Potential of Clean Mercury and the Influence of Gases and of the Circulation of the Mercury upon it — WAYNE B. HALES 950

Thermionic Emission from Clean Platinum — LEE A. DUBRIDGE 961

Electrical Resistance and Magnetic Permeability of Iron Wire at Radio Frequencies — G. R. WAIT, F. G. BERKEWEDDE, AND E. L. HALL 967

On Free and Bound Electrons in Metals — RICHARD RUEDY 974

Anomalous Dispersion, Absorption and Kerr Effect in Viscous Dielectrics — DONALD W. KITCHIN AND HANS MÜLLER 979

Effect of Diffraction around the Microphone in Sound Measurements — STUART BALLANTINE 988

On the Origin of the Aurora Polaris — S. CHAPMAN 993

Reply to the Criticism by S. Chapman — E. O. HULBURT 996

Electronic States and Band Spectrum Structure in Diatomic Molecules VII. $^1P \rightarrow {}^1S$ and $^1S \rightarrow {}^1P$ Transitions. A Correction — ROBERT S. MULLIKEN 997

Book Reviews 998

Index to Volume 32 1001

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THE

PHYSICAL REVIEW

ABSOLUTE X-RAY WAVE-LENGTH MEASUREMENTS

By A. P. R. Wadlund

Abstract

Wave-length of the $K\alpha_1$ lines of Cu, Fe, and Mo as determined by a speculum metal grating.—By means of a speculum metal grating, 50 lines to the mm, ruled over a length of 5 mm, the wave-lengths of the $K\alpha_1$ line of copper, iron and molybdenum were determined as 1.5373 ± 0.0008, $1.937(6) \pm 0.002(3)$ and $0.708(3) \pm 0.001(1)$ angstroms respectively. Using the $K\alpha_1$ line of copper the following constants were calculated: the *grating space of calcite* 3.0290 ± 0.0016A, *Avogadro's number* $(6.061 \pm 0.009) \times 10^{23}$ molecules per gram molecule, and the *electronic charge* $(4.774 \pm 0.007) \times 10^{-10}$ e.s.u. A discussion is given of the sources of error involved, of which the most important are those due to the settings on the lines of the diffraction pattern and those due to the inexact setting of the grating.

Introduction

As a result of their work on the diffraction of x-rays by a ruled grating, Compton and Doan[1] made the statement that they saw "no reason why measurements of the present type may not be made fully as precise as the absolute measurement by reflection from a crystal, in which the probable error is due chiefly to the uncertainty of the crystalline grating space." The present investigation was undertaken with the view of getting more precise measurements by this method than is at present possible by the crystal method.

Theory

As was shown by A. H. Compton[2], x-rays are totally reflected from a plane surface when the angle of incidence is sufficiently large. If then, the glancing angle is less than the critical angle for total reflection, a reflection grating may be used for diffracting x-rays and the usual formula of optics holds, viz.:

$$n\lambda = D(\sin i + \sin \phi) \tag{1}$$

where i is the angle of incidence, ϕ is the angle of diffraction for order n, and D is the grating space. Eq. (1) may be written in terms of the glancing angles:

$$n\lambda = D[\cos \theta - \cos (\theta + \alpha)] \tag{2}$$

[1] A. H. Compton and R. L. Doan, Nat. Acad. Sci. 11, 598 (1925).
[2] A. H. Compton, Phil. Mag. 45, 1121 (1923).

where θ is the glancing angle of incidence, $\theta+\alpha$ is the glancing angle of diffraction for order n, and hence α the angle between the zero order and the nth order. For the small angles involved it is more convenient to use Eq. (2) in the form

$$n\lambda = D(\alpha\theta + \tfrac{1}{2}\alpha^2 - 4\text{th degree terms} + \text{etc.}) \qquad (3)$$

It was found unnecessary to use the 4th and higher degree terms in the present work.

For their more precise diffraction measurements, Compton and Doan used monochromatic radiation, as for example, $K\alpha_1$ of Mo. Thibaud[3] has been able to get beautiful diffraction patterns using general radiation, the complete spectrum being clearly separated and sharp. The method used in the present instance follows closely that of Compton and Doan, rather than that of Thibaud.

Arrangement of Apparatus and Experimental Procedure

The arrangement of the apparatus is shown diagramatically in Fig. 1. A water cooled metal tube X with changeable target and filament was used as the source of x-rays. The general radiation passed through slit S_1, and the particular line whose wave-length it was desired to measure was reflected

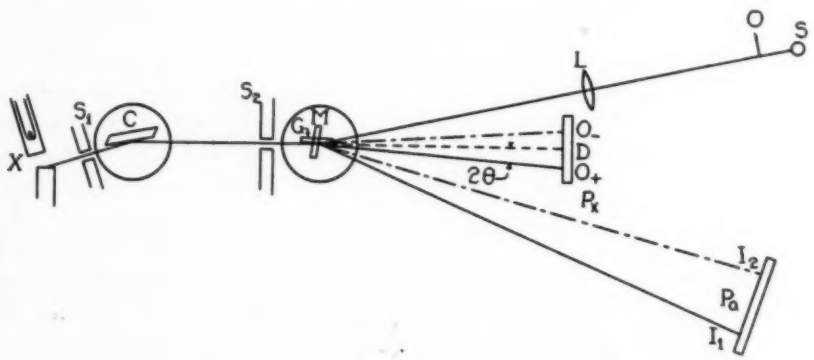

Fig. 1.

from the calcite crystal C. Several crystals were tried and that one used which gave the sharpest lines. The crystal was mounted on a table which could be rotated by a slow motion screw. The monochromatic radiation was then collimated by the slit S_2 about 1/10 mm wide before striking the grating G. The slit S_2 was so designed as to be capable of horizontal motion perpendicular to the x-ray beam and rotation about a vertical axis and a horizontal axis parallel to the beam. The grating was held in place by 3-point contact screws which allowed of considerable adjustment. This holder was in turn mounted on a table which could be moved in two mutually perpendicular directions (parallel to and perpendicular to the beam of x-rays) by slides which were

[3] J. Thibaud, Rev. d'Op. 5, 105 (1926); Phys. Zeits. 29, 241 (1928) (and elsewhere).

actuated by very fine pitch screws. The slides and grating were then placed on a table such as used for the crystal, so as to be capable of rotation about a vertical axis. The whole arrangement was then attached to a carriage which was capable of motion by a screw in a horizontal direction perpendicular to the beam. The diffraction pattern was recorded on the photographic plate P_x. For the purpose of angle measurement a plane-parallel mirror M was mounted on an arm which extended a few cm above the grating and moved as an integral part of the rotating part of the table. The mirror M was so mounted as to be capable of motion of translation along two horizontal directions and rotation about a vertical axis. The mirror could also be tilted giving in essence a motion of rotation about a horizontal axis. As a means of measuring angles through which the grating was rotated, a straight edge O served as an object, the image being formed at P_a where it was photographed.

The actual manipulations involved in obtaining the photographs at P_a and P_x are given in what follows. Having obtained monochromatic radiation through the slit S_2, the grating was carefully aligned photographically, so that the beam which struck the grating was split by the face of the grating at zero glancing angle, the object being to allow of total reflection from two positions approximately 180° apart. The positions of the grating which were to be used were then determined, after which the mirror M was carefully adjusted. The dotted line GD (Fig. 1) is the direct beam; GO_+ the reflected beam from the face of the grating as shown, called positive zero for short; the dot-dash line GO_- the reflected beam in the second position, called negative zero. On the plate P_a, I_1 corresponds to O_+, I_2 to O_-. With this arrangement no negative order was necessary for determining the glancing angle, nor was it necessary to measure the indeterminate distance from the plate P_x to the effective part of the grating. After this preliminary work the actual photographs to be measured were obtained in the following manner. The grating was first moved out of the beam and a short exposure of the direct beam recorded on the film P_x. This place on the film was then protected from further immediate exposure with a strip of lead and the grating moved back to its predetermined position and a short exposure taken to record the negative zero order. The position of the grating was then recorded by an exposure on plate P_a, after which the grating was turned and the positive position recorded. Sufficient time was allowed for the recording of the positive zero order, then the direct beam was uncovered and a lead frame placed in front of the film so that only the central portion of the plate was exposed to the action of the x-rays. When the exposure had been going for a time sufficient to record several orders of the spectrum, and before the plate P_x was removed, a check on the glancing angle was obtained by putting another plate at P_a, recording the position of the grating, then rotating back to get a second negative zero order, the position of which was also determined. When copper or iron radiation was used, there were placed in the paths CS_2 and GD, tanks which could be evacuated, in order to reduce the absorption of these radiations. All parts of the apparatus were rigidly fastened to a concrete pier. The room temperature did not vary more than 1°C during an exposure.

Results

Fig. 2 is an enlargement of a film obtained at P_z, and is typical. It was obtained for $K\alpha_1$ of Cu at a glancing angle of 21′:19″.5 after an exposure of about 30 hours at a distance of approximately 1 meter. The tube was operated at about 30 KV peak. The two negative zero orders are shown at O_-, direct beam at D, positive zero order at O_+, two negative diffracted orders

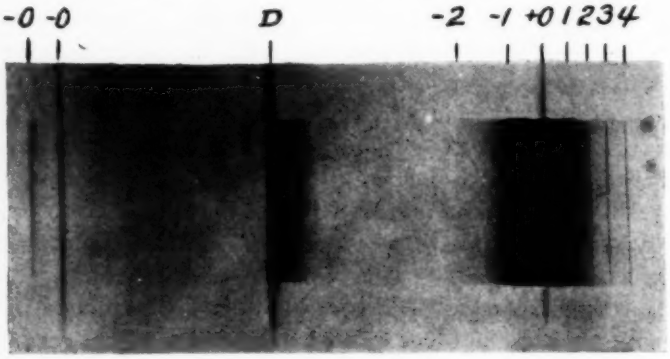

Fig. 2.

at -2 and -1, and four of the six measurable positive diffracted orders at 1 to 4. The 6 positive orders are visible and measurable on the original negative. The broad beam beside D is that part of the direct beam which passed the grating. Fig. 3 shows the type of plate obtained at P_a, the distance MI being about 2 meters.

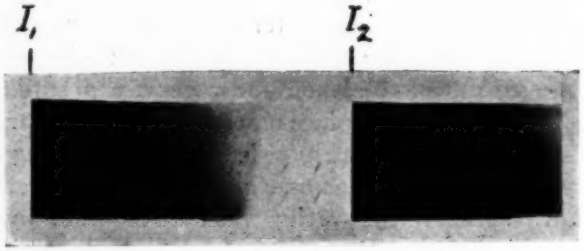

Fig. 3.

Referring to Fig. 1, if $I_1I_2=c$, $MI=d$, $DO_-=a$, $DO_+=b$, $c/d=m$, and $a/b=l$, then

$$\tan 2\theta = m/(l+1) \tag{4}$$

to the degree of accuracy required. Having determined θ it is an easy matter to determine from the measurements $\theta+\alpha$ and hence α. Measurements of the plates P_z and P_a were made on two comparators on different days and results of different observers used. The only distances not measured on the comparator were MI and the grating space. The former was measured by making fiducial marks on a steel tape and comparing the distance between

these marks with a standard meter. The grating space was determined with a Geneva spectrometer using the green line of mercury.

The grating used to obtain the diffraction patterns which form bases of measurement throughout this report was of speculum metal. The rulings were 2 cm long and extended over a distance of only 5 mm, the grating space being 2.0000×10^{-3} cm. It was ruled by Mr. Fred Pearson on one of Professor A. A. Michelson's ruling engines and was particularly free from ghosts.

The results obtained from measurements of the plates are given below.

$$\text{Cu } K\,\alpha_1 = 1.5372(5) \pm 0.0003(3)\text{A}$$
$$\text{Fe } K\,\alpha_1 = 1.9376(6) \pm 0.002(1)\text{A}$$
$$\text{Mo } K\,\alpha_1 = 0.7083 \pm 0.0006\text{A}$$

The probable errors are those estimated from the errors in the measured distances involved as explained below. The Cu wave-length is the weighted mean of measurements on two plates showing 6 and 3 orders respectively. The glancing angles of incidence being 0°:21′:19″.5 and 0°:18′:51″.6 respectively. The wave-length for Fe is the result of a calculation on only 1 positive order, the glancing angle of incidence being 0°:23′:38″.0. Although the lines of the plate were not as sharp as on plates for Cu and Mo, the angles were of such magnitude as partly to offset this circumstance. The Mo wave-length is the weighted mean of three measurements on first order spectra only at glancing angles of 0°:7′:55″.6 and 0°:7′:57″.5 and 0°:10′:5″.3. The sharpness of the lines seems to warrant recording the results.

Discussion of the Probable Error of the Results

1. *Errors due to measurements.* The probable errors given in the above table were obtained from Eq. (6) given below. This expression is derived in order to show how the measurements made for wave-length calculation actually enter. Let the symbols used have the significance of those used in Figs. 4 and 5.

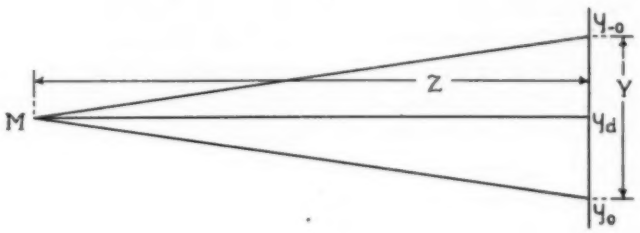

Fig. 4.

A simple calculation shows that Eq. (3) becomes to the degree of approximation required for the calculation of the probable error

$$\lambda = \frac{D}{2n}\left(\frac{\xi_n \zeta_n}{X^2}\right) \qquad (5)$$

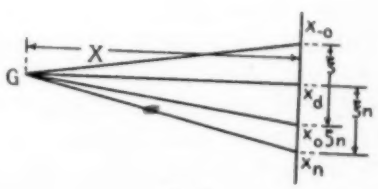

Fig. 5.

Hence we take as the probable error in the wave-length as calculated from the nth order

$$PE\lambda_n = \frac{D}{2n}\left\{\left(\frac{\zeta_n+\xi_n}{X^2}\Delta x_n\right)^2+\left[\frac{\xi_n}{X^2}\left(1+2\frac{\zeta_n}{\xi}\right)\Delta x_0\right]^2+\left(\frac{\zeta_n}{X^2}\Delta x_d\right)^2 + \left(2\frac{\zeta_n\xi_n}{X^2\xi}\Delta x_{-0}\right)^2+\left(2\frac{\zeta_n\xi_n}{X^2Y}\Delta Y\right)^2+\left(2\frac{\zeta_n\xi_n}{X^2Z}\Delta Z\right)^2\right\}^{1/2} \tag{6}$$

We thus have the probable error of a wave-length determination given in terms of the measurements used in the calculation of this wave-length, the Δ^* signifying the probable error of the measurement*.

The error involved in using Eq. (5), which is an approximation, is equivalent to neglecting—under the radical of Eq. (6)—coefficients of the Δ's in which X^4 enters in the denominator. It is evident that this introduces no appreciable change in the probable error as given by Eq. (6).

In all plates obtained ζ_n was of the order 1/10 to 1/3 ξ_n. Consequently, if the probable error of a setting on x_n, x_0, x_d, x_{-0}, y_0, y_{-0}, (ΔY being equal to $[(\Delta y_0)^2+(\Delta y_{-0})^2]^{1/2}$) are about equal, the most important factors are the first and second; in other words, the most important settings are x_n, and x_0. The probable errors of settings on the various lines of a single plate varied at times by a factor of 3.

As an illustration of the data used in the calculations, the 4th order of the film showing six orders is taken.

$\xi=2.4010$ cm, $Y=4.7850$ cm, $Z=204.00$ cm, $\xi_4=1.6596$ cm, $\xi_0=1.2700$ cm From these data $X=102.362$ cm; $\theta=0°:21':19''.5$; $\alpha_4=0°:13':4''.9$; $\lambda_4=1.5423$A. For the calculation of the probable error the following additional data are given: $\Delta x_d=\pm0.00007$, $\Delta x_0=\pm0.00006$, $\Delta x_{-0}=\pm0.00007$, $\Delta x_4=\pm0.00018$, $\Delta Y=\pm0.00011$, $\Delta Z=\pm0.01$, $\zeta_4=0.3896$. Hence $PE\lambda_4=\pm0.0009$A.

2. *Consideration of approximations used.* The approximation used in the probable error has been considered above. The statement that it was found unnecessary to use the 4th and higher degree term of Eq. (3) was verified by actually including these terms. That Eq. (4) gives accuracy of the degree required is evident from the following considerations. In deriving Eq. (5) the relation $X=(x_0-x_{-0})Z/(y_0-y_{-0})$ was used. It is easy to show from Figs. 4 and 5 that Eq. (4) is really equivalent to using this relation as though it were absolutely correct. That it is not absolutely correct is evident from the way in which plates P_a and P_x were set. P_a was placed so that it was perpendicular to the direct beam, P_x was set so that the perpendicular from the mirror to the film struck half way between the images. If x_d-x_{-0} was equal to x_d-x_0 then the above relation would be exact. This was never the case, the ratio of these distances, i.e., $(x_0-x_d)/(x_d-x_{-0})$ was always greater than 9/10 and less than 11/10. This means that the plate P_x should have been set so that $(y_0-y_d)/(y_d-y_{-0})=(x_0-x_d)/(x_d-x_{-0})$. Calculation shows that the approximation made leads to an inappreciable correction in Z and hence in X and the angles θ and α.

3. *Consideration of true errors.* There remains the consideration of true errors. Inasmuch as in x-ray work of this character only divergent and convergent beams are used, Eq. (1), which is derived for plane waves, is not strictly applicable. Porter[4] has recently derived an expression for a first approximation to the correction which Eq. (3) needs. The conditions imposed by this theory are almost exactly fulfilled in the present experimental arrangement. Calculation shows that the wave-lengths given above should be multiplied by 1.0000037. Consequently this source of error may be neglected.

Consider now the mirror M. The faces of this mirror were plane and parallel to 1/20 of a wave-length of green light which would introduce a constant error in the total angle $y_{-0}My_0$ (Fig. 4) and hence in the angle θ, assuming that the sputtering of the faces of the glass did not change their degree of parallelness. Another true error is introduced by not getting the mirror adjusted so that the two faces would be in the same plane when

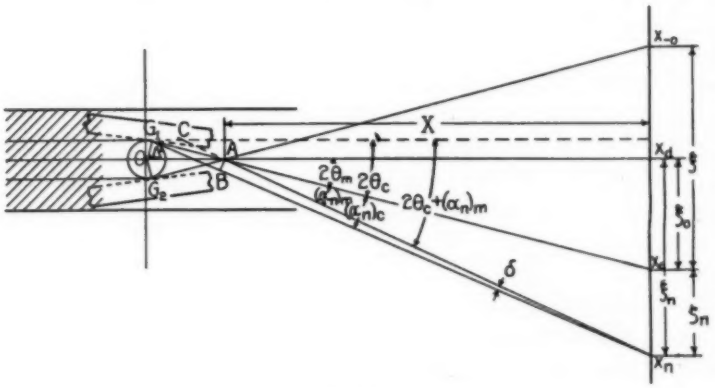

Fig. 6.

rotated through 180°. This adjustment was made to within 0.0025 cm (that is 0.001 inch). Assuming these errors to be in the same direction the error in wave-length is of course most marked in first order calculations, but well within the probable error of a single calculation.

The greatest source of error is that introduced by the inexact setting of the grating. By inexact we mean that the axis of rotation of the grating table may not have been in the plane of the face of the grating. Thus, let O (Fig. 6) be the axis of rotation of the grating table, and Δ the radius of the circle described by the center of the grating. Let G_2 be the position of the grating for obtaining the negative zero order, G_1 the position of the grating for obtaining the positive zero order and the diffraction pattern. The cross-hatched portion is the direct monochromatic beam. The subscripts c and m on the angle denote the angles as they should be (correct) and as measured respectively. From the geometry of the figure $2\theta_c = 2\theta_m$ and δ is the correction which should be made to the measured angle $(\alpha_n)_m$ to obtain the correct angle $(\alpha_n)_c$. A simple calculation shows that:

[4] Alfred Porter, Phil. Mag. 3, 1067 (1928).

$$\delta \doteqdot \frac{\Delta}{X}\frac{\zeta_n}{\xi_0} \tag{7}$$

We now define ϵ by

$$\delta = \epsilon(\alpha_n)_m \tag{8}$$

so that

$$(\alpha_n)_c = (\alpha_n)_m(1+\epsilon) \tag{9}$$

Dropping the subscript on the angle θ and the subscript n on the angle α, we have from Eq. (3) $n\lambda_c = D(\alpha_c\theta + \frac{1}{2}\alpha_c^2)$ where λ_c is the correct wave-length. Using Eq. (9) we get $n\lambda_c \doteqdot n\lambda_m + D\epsilon(\alpha_m\theta + \alpha_m^2)$ i.e. the error in the wave-length is

$$\delta\lambda = (D\epsilon/n)(\alpha_m\theta + \alpha_m^2) \tag{10}$$

From consideration of the manner in which the grating was aligned the probable value of Δ is about 0.0005 cm. This gives, from the data above, for the 4th order of $K\alpha_1$ of Cu, $\delta_4 = 0°:0':0''.3$; $\epsilon_4 = 0.00039$ and $\delta\lambda_4 = 0.0007$A. The same value of $\delta\lambda$ was obtained for all orders of both plates used for the calculation of $K\alpha_1$ of Cu. The values of $\delta\lambda$ for $K\alpha_1$ of Fe and $K\alpha_1$ of Mo were ± 0.001 and ± 0.0009 respectively. The $\pm$ sign is used to allow for the possibility of the grating "running past" the center position by an amount Δ, Fig. 6 shows the grating "running short" by this amount.

Conclusions

1. *Wave-lengths of $K\alpha_1$ of copper, $K\alpha_1$ of iron, $K\alpha_1$ of molybdenum.* The final results for the wave-lengths of $K\alpha_1$ of Cu, $K\alpha_1$ of Fe, and $K\alpha_1$ of Mo are as given below, the column at the right being the values taken fromSiegbahn.[5]

Cu $K\alpha_1 = 1.5373 \pm 0.0008$	1.53730A
Fe $K\alpha_1 = 1.937(6) \pm 0.002(3)$	1.93230A
Mo $K\alpha_1 = 0.708(3) \pm 0.001(1)$	0.70759A

2. *The crystal grating space of calcite.*[6] The crystal grating space using the wave-length of $K\alpha_1$ of Cu given above is calculated as follows. If we let the subscript 1 denote the value of the various quantities as used in crystal wave-length determinations we have $d = d_1\lambda/\lambda_1$ where d is the crystal grating space (calcite in the present experiment). Taking $d_1 = 3.02904$A and $\lambda_1 = 1.53730$A we obtain

$$d = 3.0290 \pm 0.0016\text{A}$$

3. *Avogadro's number.* If we let N represent Avogadro's number, then

$$N = \frac{nM}{\rho d^3\phi(\beta)} = \frac{nM}{\rho d_1{}^3\phi(\beta)}\left(\frac{\lambda_1}{\lambda}\right)^3 = N_1\left(\frac{\lambda_1}{\lambda}\right)^3$$

[5] "The Spectroscopy of X-rays" (Ox. Univ. Press 1925) p. 105.

[6] Since the preliminary publication of these results (A. P. R. Wadlund, Proc. Nat. Acad. Sci. July, 1928) a paper by E. Bäcklin (Inaugural dissertation, Uppsala Universitets Arsskrift 1928) has come to my attention in which he determines the grating space of calcite from grating measurements on the Kα line of aluminum. He finds d = 3.033 ± .003A.

where n represents the number of molecules in each elementary rhombohedron, M is the molecular weight of calcite, ρ is the density of calcite, $\phi(\beta)$ is the volume of rhombohedron the distance between whose opposite faces is unity and the angle between whose edges, β, is that between the axes of the crystal.

Hence, if we take $N_1 = 6.061 \times 10^{23}$ we get

$$N = (6.061 \pm .009) \times 10^{23} \text{ molecules per gram molecule.}$$

4. *The charge on the electron.* We obtain the electronic charge e from

$$e = \frac{Mc}{10Nz} = \frac{Mc}{10N_1 z}\left(\frac{\lambda}{\lambda_1}\right)^3 = e_1\left(\frac{\lambda}{\lambda_1}\right)^3$$

where M is the molecular weight of silver, let us say, z its electrochemical equivalent, and c is the velocity of light. If we take $e_1 = 4.774 \times 10^{-10}$ e.s.u. there results

$$e = (4.774 \pm .007) \times 10^{-10} \text{ e.s.u.}$$

It will be seen that these values of N and e are only slightly less precise than those determined by Millikan's oil drop measurements (6.061 ± 0.006 and 4.774 ± 0.005 respectively) and that they agree exactly with those determinations.

This experiment was undertaken at the suggestion of Professor A. H. Compton whom the writer wishes to thank for his keen interest and for the valuable suggestions he has made. Acknowledgment of the suggestions of Dr. J. A. Bearden is also made and indebtedness is due Dr. R. L. Doan who had designed much of the apparatus before the writer started work. An expression of thanks is also extended to Professor and Mrs. G. S. Monk who made measurements on some of the plates.

RYERSON PHYSICAL LABORATORY,
UNIVERSITY OF CHICAGO.
August 24, 1928.

A NEW HIGH POTENTIAL X-RAY TUBE

By C. C. Lauritsen and R. D. Bennett*

Abstract

An attempt has been made to develop apparatus and methods of operation for generating and investigating x-rays in the region beyond 300 kv. A tube is described which was designed to operate with 1000 kva, one million volt, transformers available at the California Institute of Technology. The tube is built up of glass cylinders internally shielded against electronic bombardment. The pheonomenon of "cold emission" is utilized for obtaining the electrons, the full potential being applied between electrodes of suitable curvature placed close together, (1 to 2 cm). A preliminary report of the results is given. This includes oscillograms showing the peculiarities of the current due to "cold emission" as well as the actual potential across the tube. Absorption measurements of the x-rays have been made with lead up to 2 cm thick and it is shown that secondary emission plays an important part in the photo-chemical action of these rays. Satisfactory operation has been obtained up to 750 kv.

Introduction

THE present paper is a preliminary report of the work done on the construction and operation of a high potential x-ray tube intended for investigating the radiation beyond about 300 kv.

Although no satisfactory quantitative analysis has as yet been completed we have thought it advisable to present the present paper at this time because one of us is leaving the Institute to take up other work elsewhere. It is expected, however, that the work will be continued here.

When this work was undertaken very little had been done to investigate the radiation produced by x-ray tubes at potentials above about 300 kv. Of the several reasons for this one of the most important is the expense and difficulty connected with the construction and maintainance of a satisfactory source of high potential. The apparatus necessarily becomes very large if one wishes to operate at commercial frequencies, not only because of insulation difficulties but also because great power is required merely to maintain the potential. Thus in the present apparatus the charging current at 750 kv amounts to 300 ma or 225 kva.

A second difficulty is the construction of the tube. If it is to be used in air it must be large to prevent external flash-over along the glass. Even if submerged in oil or otherwise protected it must be of large dimensions in order to maintain large clearance and large radii of curvature of the metal parts inside.

At sufficiently high potential gradient the metal parts give off an apparently unlimited supply of electrons and it is essential that these electrons be prevented from striking and puncturing the glass.

In the present tube this emission from the cold metals is utilized for producing the x-rays, no other source of electrons being required. The stray

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electrons are stopped by metal shields and conducted to ground by means of high resistance leaks shunted by suitable condensers.

The use of cold emission as a source of electrons in the production of x-rays has been attempted at lower potentials both in this laboratory and by Lilienfeld, but the operation has always been too erratic for practical use. At high potential this objection is not very important in the present instance.

Equipment Available

The source of potential consists of the 1000 kv, 1000 kva transformer set of the California Institute of Technology, together with its control equipment. The set, designed by R. W. Sorensen,[1] consists of four units connected in cascade (see Fig. 1). Each unit has three windings. Two of these are rated

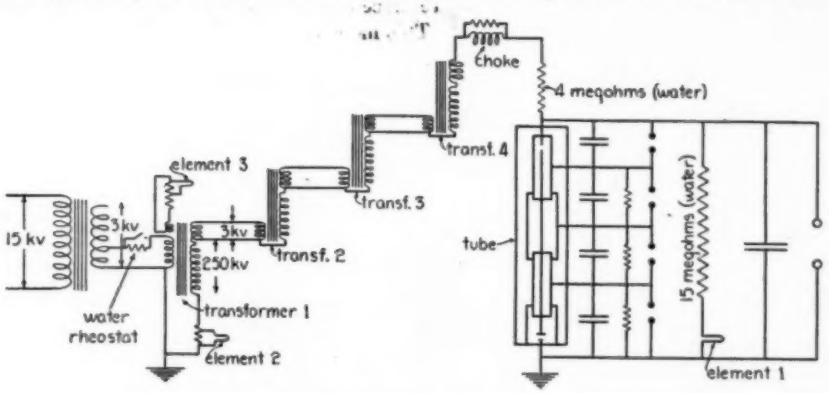

Fig. 1. Diagram of transformer set.

at 1000 kva at 3000 volts, one being connected to the case and the other insulated from core and case for 250 kv. Connected between these windings is the 250 kv winding. The case of each unit is insulated from ground for its respective potential.

This transformer set is housed in a room 64×138 by 50 ft high, the last three transformer with their insulating supports being placed in a pit in order to get sufficient overhead clearance.

The Tube

A sketch of the tube itself is given in Fig. 2. The supporting structure consists of a tower 14 ft. high and 8 ft. square at the base, constructed of redwood timber crossed and braced to give rigidity. The bed plate of the tube consists of a piece of boiler plate 28×28×0.5 in. bolted to this platform. This plate has a hole 16 in. in diameter over which fits a water-cooled disk of 7/8 in. boiler plate making a foundation for the tube proper, and carrying the pump tubes and one of the water cooled electrodes.

The glass consists of cylinders each 12 in. in diameter and 28 in. long of the kind used in gasoline dispensing pumps. The lowest cylinder is set on a rubber gasket in a groove in the end plate and the other joints are made similarly in grooves in steel rings, leaks being prevented by coating the joints outside with

[1] R. W. Sorensen, Journal A.I.E.E. **44**, 373 (1925).

shellac after the tube is assembled. The steel rings also support the internal shields. These are of steel 1/16 in. thick alternately of 11 in. and 7 in. diameter overlapping about 4 in. at the ends. At each end of each shield is a ring of 1 in. diameter steel tubing to eliminate sharp edges. All joints are welded and carefully smoothed.

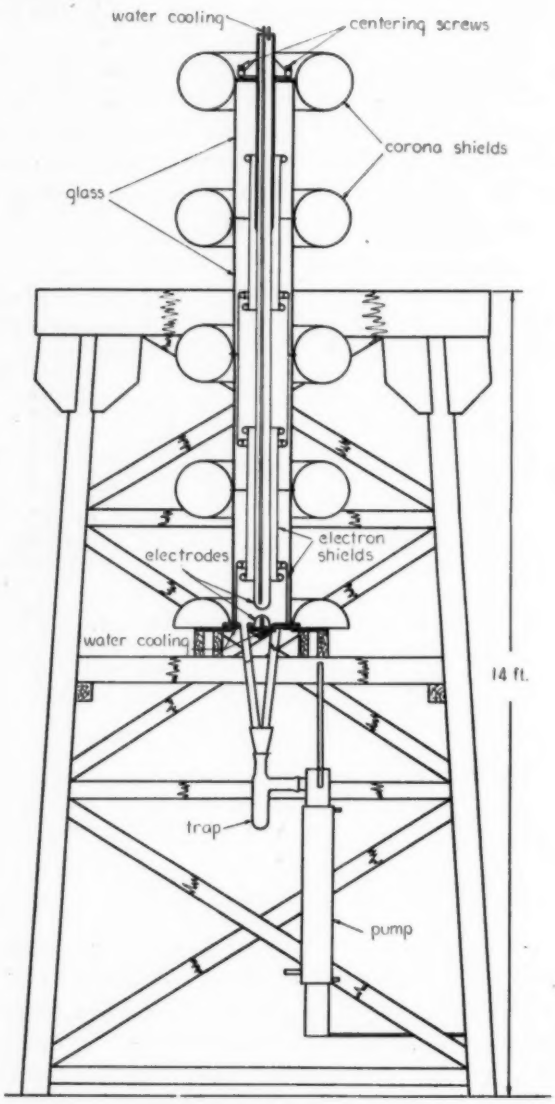

Fig. 2. Sketch of the tube.

The upper electrode consists of a three-inch diameter steel tube reaching to within four inches of the bed plate. The upper three feet of this tube has a 0.25 in. wall to give rigidity. It is supported in a circular cover plate of steel 0.5 in. thick with an arrangement of screws for flexing this plate in order to center the lower end of the electrode.

Each joint ring is equipped with an outside corona shield of tin foil covered papier-mache, in the shape of a torus whose circular section is one foot in diameter.

The lower end of the upper electrode has been given a variety of shapes including a steel cone with a rounded point, a three-inch steel hemisphere and the steel hemisphere equipped with points of steel and tungsten of various sizes. The lower electrode has had the form of a five-inch steel hemisphere concave upward, a flat plate of copper, with or without tungsten point, and a three-inch steel hemisphere convex upward. Both electrodes were water-cooled in all cases.

An idea of the form and position of the actual target for some of these electrode arrangements may be obtained from the pin-hole camera photographs, shown in Fig. 3.

Fig. 3. Pinhole camera pictures with various electrode arrangements.

Controls

Power is supplied to the set of high potential transformers through induction regulators, the primaries of which are wound for 15,000 volts and the secondaries give any potential between 0 and 3000, the variation being continuous. These regulators and the necessary oil switches are normally controlled from either of two desks in the laboratory, but for the present experiment the controls have been extended to a service tunnel placing about six feet of concrete and several feet of earth between the operators and the tube, for protection against the radiation.

In the 3000 volt circuit is placed a water-break switch. This switch is so constructed that when open, it leaves sufficient resistance in the circuit to limit the potential on the tube to about 250 kv. When closed this resistance is cut out and the potential is raised to any chosen value. This arrangement removes the danger of destructive transients occurring in the transformers as a result of switching. The closing mechanism of the water-break switch is controlled through a contactor by a timing device by means of which it is possible to vary at will the number of closings per minute and the duration of each closing.

After the tube has been operated for some time it is possible to run it at high potential one second in eight, without raising the gas pressure beyond the capacity of the pumps or producing excessive heating of the electrodes.

Pumps

The rough pump consists of a Cenco Megavac. Ahead of this are two stages of the usual size mercury diffusion pumps of glass. Next is a diffusion

pump built of steel with welded joints, having an annular nozzle 5 in. in diameter. A 2 in. side tube leads to the liquid air trap which is made of 3 in. diameter glass tubing. From the top of the trap three 1.5 in. diameter steel tubes connect to the lower end plate of the tube, the upper side of the holes being properly rounded and smoothed.

With this equipment it is possible to produce and maintain a pressure of less than 10^{-5} mm of Hg, i.e. below the range of the McLeod gauge. That this pressure is sufficiently low for the present purpose is due to the fact that the electrodes are comparatively close together so that by far the greater number of electrons travel only a short distance and consequently have a correspondingly smaller chance to produce ionization.

Protective Rheostat

The tube is connected to the transformers through a protective rheostat having a resistance of about 4 megohms and consisting of 50 ft. of 0.5 in. hose hung in a spiral about a string of strain insulators. At each end of the spiral is a flat metal plate 6 ft. in diameter, this being necessary to equalize the field along the hose and prevent its destruction by corona. The metal plates are about 10 ft. apart, the upper one being some 20 ft. from the ceiling. Water to the rheostat flows up through a hose to the ceiling, then drops in a broken stream to a bucket on top of the upper plate, then through the rheostat hose and through the upper electrode of the tube from which it drops 20 ft. to the floor, the broken stream providing sufficient insulation.

Measurements

Potential measurements. Several methods are available for measuring the potential actually applied to the tube, and several have been used with more or less success. By far the most satisfactory and illuminating for the present purpose is the record obtained by means of an oscillograph, as it gives not only the maximum potential, but also the rapid fluctuations characteristic of this particular method of operation. The oscillograph used is a three-element General Electric Type E-M Form C.

One of the oscillograph elements is connected between the high-potential end of the tube and the ground through a resistance of about 15 megohms. This resistance consists of about 75 ft of 3/8 in. diameter rubber tubing through which tap water is circulated.

A calibrated spark-gap is placed directly across the tube. This gap is usually set somewhat above the operating potential and thus serves as a limiting device.

A second element of the oscillograph is connected across a special winding on the core of the first transformer, thus recording the potential of this transformer which is quite accurately one-fourth of the total potential of the set.

In addition the first transformer is equipped with a device for measuring the charging current to the condenser bushing. This current is rectified by means of two small Tungar tubes and then measured on a d.c. milliammeter which is calibrated to read in volts directly.

Current measurements. Here again the oscillograph provides the most satisfactory method used so far. The third element of the oscillograph is connected directly in the ground return of the transformers and therefore gives a record of the total current, i.e. the charging current as well as the current through the tube.

Radiation measurements. Two methods have been used so far for investigating the radiation, namely, absorption of the x-rays in lead and absorption in aluminum of the secondary emission from lead.

Absorption measurements were made be covering a strip of a photographic plate by a block of lead having a wedge-shaped groove and exposing at a distance of about 30 cm from the center of the source. Simultaneously four other strips cut from the same plate and enclosed in lead of uniform thickness were exposed to the radiation at distances from 50 cm up to 8 m from the source.

Fig. 4. Absorption in lead wedge 1.5 cm to 3.7 cm in thickness.

Usually the blackening of at least three of these control plates would fall within the range of the main plate, so that calculations could be made assuming only the inverse square law of intensity.

The five plates were developed simultaneously and measured on a recording microphotometer, all five traces being put on the same record. From this record one can then measure directly that thickness of lead which has reduced the intensity to any desired fraction and thus obtain the necessary data for determining the absorption coefficient and wave-length. An example of such a plate is shown in Fig. 4.

In order to be able to load these plateholders in daylight the plates were wrapped in black paper. This wrapping was found to influence the blackening

Fig. 5. Secondary emission from various elements behind 3 mm of lead.

to such an extent that one is forced to the conclusion that the photo-chemical action in the case of these hard x-rays is due primarily to secondary emission from the plateholder rather than to the direct action of the rays themselves.

In order to investigate this point the sensitive side of a photographic plate was covered with small pieces of various metals in the form of thin sheets and

then placed behind 3 mm of lead and exposed for about 30 seconds at a distance of 50 cm.

The blackening was found to increase greatly with the atomic number of the metal in contact with the emulsion, being very weak in the case of aluminum and very strong for lead. (See Fig. 5.)

The absorption in aluminum of the secondary emission from lead was shown by interposing a step-wedge made up of ten layers of 0.001 cm aluminum foil between the lead and the emulsion of the photographic plate.

The blackening of the plate decreases noticeably for each additional layer, all ten steps being plainly visible. This is shown in Fig. 6.

Pb

Fig. 6. Step wedge of Al each step being 0.001 mm.

It was found to be immaterial whether the sensitive side of the plate was turned toward or away from the tube.

A magnetic spectrograph for analysing this secondary emission has been set up but no results have been obtained up to this time.

Operation of the Tube

The action of the tube seems to be somewhat as follows. The potential during any particular cycle builds up to a certain critical value at which a crater breaks in the negative electrode.[2] This crater then emits an unlimited number of electrons, amounting to a complete and exceedingly fast short circuit which not only reduces the potential at once to zero, but, because of the inertia of the circuit, actually reverses the potential across the tube. As soon as the potential can build up again the process is repeated, from one to fifty craters being broken during each half cycle. The critical potential and the asymmetry of the wave depend on the size, shape and materials of the electrodes and on how thoroughly they have become outgassed. Trace 1 on Fig. 7 shows a record of the potential across the tube.

Fig. 7. Record of potential and current fluctuations.

[2] C. C. Lauritsen and R. A. Millikan, Phys. Rev. 31, 914 (1928).

All attempts to obtain an oscillogram of the current directly through the tube with the instrument at hand were unsuccessful, the surges being too fast to be recorded, and too violent to be sufficiently reduced for the instrument by any reasonable amount of shunting. Apparently thousands of amperes are involved in these rushes of current, for a neon tube connected at both ends to the steel pump structure and laid alongside it still glows whenever a surge occurs. Consequently the oscillograph was put in the circuit at the low end of the transformers, the transformers, and the protective rheostat serving to limit the current in the surges. The resulting current is shown in the second trace of Fig. 7, the wave consisting of the electron current superimposed upon the charging current of about 300 ma necessary to maintain the potential of the transformers and connections.

Conclusion

So far satisfactory operation has been obtained up to 750 kv without outgassing the metals by any heating other than that incident to the operation. There is every reason to believe that the present limit is determined by the character of the electrodes and other metal parts of the tube and can be increased considerably by proper choice and treatment of these parts. The stray electrons can be rendered harmless by shielding, and the potential can be distributed between several sections by suitable capacities and leaks from the shields to the ground. By the use of fast pumps it is possible to produce a sufficiently good vacuum with the construction used. The radiation is very powerful and can be observed by means of a fluoroscope at a distance of 100 meters. Considerable blackening of a photographic plate is produced through 2 cm of lead. The photographic action is found to be due mostly to secondary emission which is strongly absorbed in aluminum.

In conclusion we wish to express our thanks to Dr. Millikan for his interest in the problem and for appropriating the necessary funds for carrying out the work and to Professor Sorensen for his cooperation and for putting the equipment of the high potential laboratory at our disposal. To Mr. Julius Pearson, chief instrument maker, is due our thanks for many helpful suggestions and valuable assistance in constructing the apparatus.

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August, 1928.

NUCLEAR MOTIONS ASSOCIATED WITH ELECTRON TRANSITIONS IN DIATOMIC MOLECULES

By Edward U. Condon

Abstract

The question of nuclear motions associated with electron transitions is discussed from the standpoint of quantum mechanics. It appears that Heisenberg's indetermination principle gives the clue to the inexactness of the earlier method based on Franck's postulate since its strict application calls for a violation of the principle. The existence of an entirely new type of band spectrum due to the wave nature of matter is predicted and the interpretation of Rayleigh's mercury band at 2476–2482 A.U. as of this type is suggested. Finally it is shown that while Franck's postulate is also true for electron jumps in atoms, it is of but trivial interest because its inexactness is much greater for the electrons than for heavy nuclei.

TWO years have elapsed since Franck proposed a mechanism for the direct dissociation of molecules by light absorption[1] and since the extension of that mechanism to a theory of intensity distribution in band systems was made.[2] In the meantime the theory has been applied with gratifying success to the discussion of a number of band systems which have been recently analyzed. It has also been possible to derive the postulate underlying Franck's idea from the new quantum mechanics and thus to bring it into closer relation with the basic principles of quantum physics.

The first publication of this connection with quantum mechanics was very brief.[3] Since the connection provides one of the more easily visualised applications of quantum mechanics and because of the rather wide applicability of the method in molecular problems it is therefore proposed here to give a fuller account of the connection. Besides providing a justification of Franck's assumption, the quantum mechanical method provides a distinct advance since it gives, in principle at least, an exact method for calculating intensities. This is illustrated particularly neatly in cases where absorption of light results in direct dissociation of the absorbing molecule (Cl_2, Br_2, ICl). It appears that the reason Franck's postulate gives only the most probable transitions and not the range of allowed transitions near the most probable is intimately connected with the so-called uncertainty principle of Heisenberg and Bohr. The quantum mechanical treatment also points to the possible existence of a new type of molecular band structure which is a direct manifestation of the de Broglie wave-length in the spectrum of a molecule.

§1. Franck's Postulate

According to the theory of band spectra the molecule exists in different electronic energy levels. Associated with each of these is an effective law of

[1] Franck, Trans. Faraday Society **21**, part 3 (1925).
[2] Condon, Phys. Rev., **28**, 1182 (1926).
[3] Condon, Proc. Nat. Acad. Sci. **13**, 462 (1927).

force which governs the motion of the two nuclei relative to each other and which is most conveniently described by drawing the curve which gives the energy of the molecule in the non-rotating non-vibrating state as a function of the distance of the two nuclei. In Fig. 1 we have such a pair of curves drawn for the two electronic states involved in the emission of the Swan bands of carbon.[4] The curves are inferred from the energy levels of the band spectrum. Thus the moment of inertia in a given state gives the abscissa of the minimum and the frequency of vibration gives the first coefficient in the Taylor's series for the curve around the minimum, etc.

Franck postulated that in an electron transition from a state in which the molecule is not vibrating the heavy nuclei will not be affected "momentarily." Immediately after the transition the nuclei will have the same separation as before. But this will not be, in general, the equilibrium position of the law of force for the new electronic state and therefore the molecule will start to vibrate. In other words the most probable transition from the minimum of the curve for the initial state is to that point on the curve for the final state which has the same nuclear sepration. This rule was then extended to make it applicable to transitions in which the molecule is vibrating initially as well as in the final state. One postulates that the electron transition affects neither the position nor the *momentum* directly. Then if the transition occurs while the nuclei are moving relatively, the most probable final state is that in which the position and momentum just after the transition is the same as that just before. This may be supplemented by supposing that the electron transition may occur with equal probability independently of the phase of the vibratory motion. This rule gives a definite probability for each of the possible final energies which can be communicated to the molecule.

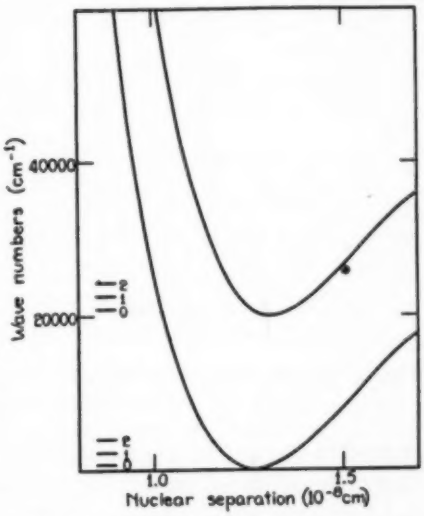

Fig. 1. Potential energy curves for the electronic states of C_2 involved in the Swan band system.

It has now to be noted that it may happen that the curves lie as in Fig. 2 (which is approximately to scale for chlorine[5]). In this case absorption of light by the non-vibrating molecule would have as the transition determined by this rule that to energy level A which corresponds to dissociation plus a perfectly definite amount of translational energy in excess of the dissociation

[4] Based on the analysis of Shea, Phys. Rev. 30, 825 (1927).

[5] The frequencies of vibration and heats of dissociation are from Kuhn, Zeits. f. Physik 39, 77 (1926). The relative position of the two curves is not known since the rotation structure of the bands has not been analyzed; their relative position as drawn here was inferred roughly from the known intensity distribution by the theory of this paper.

work, *D*. Franck first applied the method to a case of this sort—that of iodine, I_2—to explain the experiments of Dymond.[6] Experiment shows, however, that while the most favored transition is to energy level *A*, the actual absorption consists of a fairly broad continuous band. This indicates a lack of sharpness about the principle which requires explanation. Similarly in a case like Fig. 1 where the rule leads to non-dissociating transitions, its strict application leads us to predict transitions to energies in the final state which are not quantum levels. As we know that these cannot occur we are again

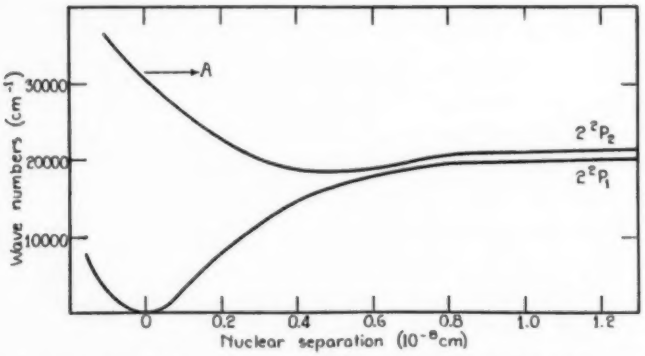

Fig. 2. Approximate potential energy curves involved in the visible absorption spectrum of Cl_2. Ordinates and abscissas as in Fig. 1.

forced to recognize a certain lack of sharpness in the rule and to suppose that the probability of transition to non-allowed levels must perhaps be assigned to the credit of the nearest allowed level.

Making such adjustments, however, the principle has proven quite useful in giving an easily visualized rule for predicting the nuclear motions set up by electron transitions. The adjustments toward looseness which have to be made in the picture are the result of a too strict application of classical ideas to the problem in hand. For a rational treatment of the problem we turn therefore to the new quantum mechanics.

§2. The Principle in Wave Mechanics

Following Schrödinger's method the behavior of a molecule is described in terms of the solution of his wave equation which involves $(3n+6)$ independent variables if n is the number of electrons in the molecule. Not much headway can be made with the equation without the application of perturbation theory. Born and Oppenheimer have shown how the problem can be handled by successive approximations amounting to an expansion in powers of $(m/M)^{1/4}$ where m is the electronic mass and M is of the order of a nuclear mass.[7] It is because of the great mass of the nuclei that one can regard their motion as determined approximately by the wave-mechanical analogue of the time-mean of the forces of all the swiftly moving electrons on the nuclei.

[6] Dymond, Zeits. f. Physik **34**, 553 (1925).
[7] Born and Oppenheimer, Ann. d. Physik **84**, 457 (1927).

Their work justifies the postulate that the coordinates of the nucleus remain approximately separable from those of the electrons in Schrödinger's theory.

We can ignore the rotation motion of the molecule. Let r be the nuclear separation and x stand for the ensemble of all the electronic coordinates. A definite state of the molecule will be characterized by e, which is the ensemble of all the electronic quantum numbers, and by n, the vibrational quantum number. The fact of approximate separability means that to a good approximation the energy of the state $E(e, n)$ is the sum of an electronic part and a vibrational part,

$$E(e,n) = E_e + E_n$$

and that the wave function for such a state $\psi_{e,n}(x, r)$ is the product of a function of the electronic coordinates and one of the nuclear separation,

$$\psi_{en}(x,r) = X_e(x) \cdot R_{en}(r).$$

Moreover the work of Born and Oppenheimer shows that the energies E_n and the function $R_n(r)$ are given by solving the one-dimensional wave equation in the variable r got by using an effective potential energy curve $U(r)$ representing the mean action of all the electrons in the state characterized by $X_e(x)$. Recently Heitler and London have obtained important results for the quantum theory of molecules concerning the curves $U(r)$ by approximations concerning $X_e(x)$. We may take empirically the $U(r)$ curve associated with each state as that one which is consistent with the quantum theory of the empirical energy levels of the band system in question.

Such empirical $U(r)$ curves in turn lead directly to solutions for E_n and $R_n(r)$ from a simple one-dimensional wave equation. The intensities of any given transition $(e', n') \rightarrow (e'', n'')$ have now to be considered. These are given unambiguously by the quantum mechanics in terms of the function $\psi_{en}(x, r)$. The electric moment of the molecule is given classically as the vector sum of the charges multiplied by their distances from a fixed point. Let $M(x, r)$ be this function. If the x are rectangular coordinates M is linear in all of the x and r. The electric moment which functions as a measure of the probability of the foregoing transition is

$$M(e',e'',n',n'') = \int \int M(x,r)\psi_{e'n'}(x,r) \cdot \psi_{e''n''}(x,r)dx\,dr.$$

One can carry out (in principle) the integration over the electronic coordinates and obtain an intermediate sort of electric moment function which is characteristic of the electron transition $e' \rightarrow e''$ and which depends only on r,

$$M(e',e'',n',n'') = \int M(e'e'',r) \cdot R_{e'n'}(r)R_{e''n''}(r)dr$$

Although the range of integration is $-\infty$ to $+\infty$ the only parts which make appreciable contributions are in the range of coordinates in which both $R(e', n', r)$ and $R(e'', n'', r)$ have values not too near zero. In such a range it

is probably always sufficient to take $M(e', e'', r)$ as a linear form $A+Br$ where it is supposed that the origin of r has been shifted to the center of the important part of the range of integration. In what follows a little brevity is gained by neglecting all but the constant part A since the reader will have no difficulty in seeing that the argument is not much affected by omitting the linear Br term. Although $M(e', e'', r)$ is unambiguously defined, almost nothing is known about it in the present state of our ignorance of the ψ functions for molecules.

We turn now to the consideration of the relative intensity of the different $n' \rightarrow n''$ transitions, associated with a definite $e' \rightarrow e''$ transition. It is a consequence of Schrödinger's theory that $R_n(r)$ will approach zero very rapidly outside of the region of the classical vibratory motion of the same energy. Inside this region it will be an oscillatory function.

From these properties of the functions $R(e, n, r)$ we read the quantum mechanical justification of the Franck postulate; together with a definite estimate of the uncertainty involved in its application. For example the $n'=0 \rightarrow n''=0$ band by the Franck rule is most probable for zero change in moment of inertia. For large change it is an improbable transition. This follows because now the wave functions $R(e', 0, r)$ and $R(e'', 0, r)$ are both Gauss error curves, each one located symmetrically about the minimum of its own potential energy curve. The over-preciseness of the rule arises from the neglect of the fact that in the zero vibration state the particle is not precisely at the minimum of the curve but has a probability of being a short distance on either side of the minimum.

One sees then that when non-oscillatory wave functions come in question the integral has the largest value when the functions overlap most. This corresponds to Franck's rule, but extended to take into account the distribution of positions characteristic of quantum mechanics. We consider next a transition from $n'=0$ to some large value of n'' for a case in which the change in moment of inertia accompanying the electron jump is small. The wave function for the large value of n'' will now be a rapidly oscillating function of r, and for this reason the integral of the product of two wave functions will be small. This corresponds to the part of the rule of §1 which says that large changes in nuclear momentum at the instant of electron transition are improbable. This comes about because the oscillatory character of the wave function is the wave-mechanical analogue of the fact that the particle has considerable momentum at that part of its orbit. (The spacing of the zeros is given approximately by de Broglie's rule, $\lambda p = h$).

The wave functions of the higher states sink rapidly to zero outside the range of the classical motion. In the neighborhood of one of the turning points they have a broad maximum—broad because here the momentum is small so the quasi-wave-length is long, and maximum because here the particle spends a larger fraction of the time than places where it moves fast. As one goes from either of the classical turning points toward the minimum of the potential energy curve, the function oscillates more rapidly and has decreasing amplitude—both things corresponding to the greater speed of the particles at this

part of the motion. We consider next a transition from the $n'=0$ state accompanied by a large change in moment of inertia. Then the vibration level which is given as most probable by the rule of §1 will be one whose wave function's broad maximum lies in a favorable position with respect to the $n'=0$ wave function and is therefore one which is favored by the wave mechanics formula. The wave functions for smaller values of n'' will not, overlap the $n'=0$ wave function, while those for larger values of n'', though they overlap, oscillate rapidly and for this reason the integral measuring the intensity is small.

Thus we see how the quantum mechanical formula agrees with the rule of §1 when that is regarded as approximate. The method of this section goes beyond that of §1 in providing exact intensity predictions and gives appreciable values to transitions in the neighborhood of those given by Franck's rule. This is an evidence of the workings of the basic uncertainty relation of Heisenberg.[4] According to this we cannot reason closely about the simultaneous values of position and momentum. One must admit uncertainties in each quantity such that their product is of the order of h. We were violating this in §1, for example where we spoke of the nuclei as having zero relative momentum when at the extremity of their classical vibratory motions. The conclusion from such a statement must, on the quantum theory, be erroneously over-precise as we have already seen is the case.

§3. The Continuous Spectrum Accompanying Dissociation

One can easily see that the quantum-mechanical formula gives the right order of magnitude for the breadth of the continuous band accompanying dissociation of a molecule. There are several good examples at present of molecules which, on absorbing light from their lowest state, dissociate into two atoms which rush apart from each other with translational energy. We will consider the examples of the halogens for which the data are available.

In Fig. 3 the curves are drawn to scale for I_2.[5] By Franck's rule the most probable transition on absorption from the non-vibrating state is the absorption of light of frequency 19000 cm^{-1}. What is found experimentally is a broad band of absorption which runs from λ4300 to λ5800. The part from λ4300 to λ4995 is continuous while from λ4995 to λ5800 it is banded. This observed range of absorption is indicated near the frequency scale in Fig. 3.

[4] Heisenberg, Zeits. f. Physik **43**, 172 (1927) and Bohr, Nature **121**, 580 (1928).

[5] Some readers may recall that the outstanding blemish in the original paper[2] was the lack of agreement between theory and experiment for the absorption bands of I_2. This was due to a bad blunder on my part in using the moment of inertia for the 26th vibrational level of the excited state thinking it was the moment of inertia for the non-vibrating molecule. For calling attention to the mistake in private communications I am deeply indebted to Professors R. T. Birge and F. W. Loomis. The curves as drawn are based on the following data:

$r'_0=3.010$	$r''_0=2.663$
$\omega^0'=127.5$	$\omega^0''=213.67$
$\beta'_0=0.02911$	$\beta_0''=0.03730$
$\alpha'=0.00017$	$\alpha''=0.00011$
$x'\omega'=0.85$	$x''\omega''=0.592$

What does the quantum-mechanical method predict for the breadth of this band? The wave function of the non-vibrating initial state is a Gauss error curve. The order of magnitude of the width of the band, as in §2, is given by the breadth of the frequency interval over which the integral for the electric moment has an appreciable value. An exact calculation would require knowledge of the form of the wave functions for the excited state. The order of magnitude involved one readily sees is about equal to the interval on the frequency scale given by "reflecting" the initial state wave function in the potential energy curve of the final state the result being curve (a) Fig. 3. Such a rough estimate of the quantum mechanical intensity integral has still to be multipled by ν^4 to give intensities. Curve (b) shows the result of doing this. It is seen that the theory predicts the *extent* as well as the position in the spectrum of the absorption quite nicely.

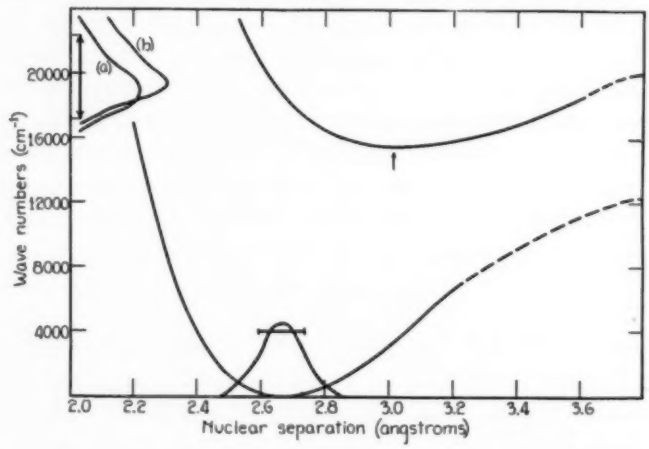

Fig. 3. Potential energy curves involved in the visible band system of I_2, together with the ψ function for zero vibration in the final state. (a) is the reflection of this ψ function in the upper state energy curve. (b) is (a) multiplied by ν^4. The two-headed arrow indicates the approximate extent of the observed absorption from the zero vibration level.

For Br_2, Cl_2, and ICl we do not at present know the moments of inertia so that we are not able to predict theoretically the exact *location* of the continuous bands accompanying dissociation. But if we put the potential energy curve for the excited state at the position which makes theory and experiment agree as to the location of the maximum then the slope comes out so in each case as to predict the observed *width* of the continuous band, at least in order of magnitude.

In Fig. 4 we have the data on the continuous absorption of Cl_2, Br_2, and ICl as a function of frequency and a line showing the theoretical width of the continuous band, as estimated in this rough way.

For Cl_2 the measurements of Halban and Siedentopf were used, for Br_2 those of Kuhn[21] for ICl those of Gibson and Ramsberger[20] while for I_2 we have only Mecke's statement[25] that the continuous begins around λ4300. The approximate theoretical values were got by regarding the potential energy

[25] Mecke, Ann. d. Physik 71, 104 (1923).

curve of the excited state as parabolic, the constant being determined by the known frequency of vibration. It was then assumed that this curve is truly so located relatively to that of the ground state as to give the empirical value of the maximum of the continuous correctly by the rule of §1. This determines the slope of the energy curve for the excited state at the equilibrium separation of the unexcited state. One can say that the true slope is certainly greater than the value estimated this way. This slope is then multiplied by the parameter, a, in the wave function of the harmonic oscillator for the normal state to give an estimate of the half-value width of the continuous spectrum on either side of the maximum, as indicated in Fig. 4 by the lines drawn just inside the absorption curves. Naturally such an approximation is

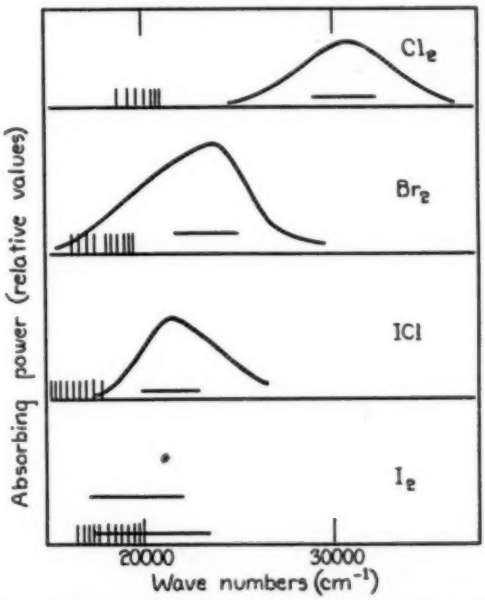

Fig. 4. The relative absorbing powers from the zero vibration state into the continuous spectrum beyond dissociation for Cl_2, Br_2, and ICl and its approximate extent for I_2 given by the lower line. The shading indicates the location of the $n''=0$ progression of bands and their high frequency convergence limits. The horizontal lines under each curve show the quantum mechanical estimate of the width of the continuous absorption. The ordinates are relative values, for each substance, so comparisons between substances are meaningless.

quite crude, but it is fair to claim that it agrees well enough with the observations to serve as support of the theory.

While this paper was in preparation Winans and Stueckelberg[11] recognized the application of these ideas to the explanation of the molecular part of the continuous spectrum of hydrogen, making use of Heitler and London's[12] quantum-mechanical potential energy curve for the 1^3S state of the molecule. Their paper serves at the same time to give not only a satisfactory account of this spectrum but also an important application of the methods of this section,

[11] Winans and Stueckelberg, Proc. Nat. Acad. Sci. **14**, (in press) (1928).
[12] Heitler and London, Zeits. f. Physik **44**, 455 (1927).

and the first empirical evidence of the physical reality of the theoretical 1^3S state of the molecule.

§4. Diffraction Bands in the Continuous Spectrum

The argument of the preceding section from the properties of the wave functions can be translated into a justification for Franck's postulate, as we have seen. Moreover it gave a quantitative understanding of the over preciseness of the conclusions drawn from the postulate by showing how the strict use of it violates Heisenberg's uncertainty principle.

The analogy with optics is a helpful one. As is well-known, geometrical optics is the analogue of classical mechanics. In the transition to wave mechanics one can regard Heisenberg's uncertainty principle as being a semi-quantitative rule which gives the order of magnitude of diffraction deviations from geometrical optics and classical mechanics respectively. The last stage of refinement is reached in optics where the wave theory is used to predict details of diffraction patterns, and in wave mechanics where Schrödinger's equation gives the exact details of the diffraction phenomena of the de Broglie waves. In this section we shall see that cases may arise in which the quantum mechanical formulas give a rippling fluctuation in intensity in the continuous spectrum accompanying dissociation.

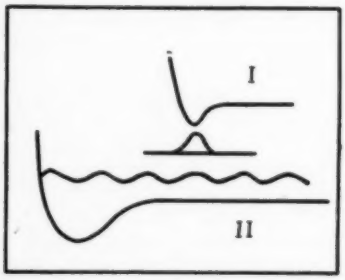

Fig. 5. Illustrating a possible relation of the two potential energy curves which would give rise to the diffraction bands.

Suppose the potential energy curves lie as in Fig. 5 where the essential point is that one curve has a very gentle slope at the abscissa values near the minimum of the other. Then by the arguments of preceding sections the most probable jump from zero vibration in electron state I to electron state II is in the continuous spectrum. By the uncertainty principle one can estimate roughly the extent of this continuous spectrum. Looking at the matter more in detail, we see that because of the gentleness of slope of curve II the Ψ functions associated with nuclear motion in this electronic state will have a rather long wave-length, so the distance between zeros might be about equal to the breadth of the Gauss error curve which is the ψ function of zero vibration in state I. We consider now the relation of the ψ_{II} functions for state II but different nuclear energies, W, to this error curve ψ_I function of state I. For values of W such that the oscillatory part of ψ lies at the same abscissa values as the maximum of the ψ_I function, the value of the integral of the product, $\psi_I\psi_{II}$ will depend very much on whether a node or a loop of the ψ_{II} function is coincident with the maximum of the ψ_I function. If a node is there, the integral will have a small value, if a loop it will be large.

We have next to consider how ψ_{II} depends on the nuclear energy W for this state. As W increases through its continuous spectrum, the ψ_{II} function will change in such a way that its wave-length gradually shortens about as $W^{1/2}$ while the positions of the zeros shift continuously past any fixed abscissa

value. This has for a consequence that the intensity of transition into the continuous spectrum will undergo a rippling variation being large for those values of W which put a loop of ψ_{II} over the center of ψ_I and small for those which put a node there. All of this effect is, of course, contained within the extent of the allowed continuous spectrum as given roughly by the Heisenberg principle; just as in optics the diffraction maxima inside the geometrical shadow of a straight edge are inside the region of diffracted light given by the uncertainty principle. Finally for large values of W the wave-length of ψ_{II} will be so small compared to the breadth of ψ_I that these maxima become less and less clearly resolved while the whole intensity sinks to zero.

With the greatest reserve I will now suggest that the peculiar band recently described by Rayleigh[13] in mercury vapor may be such an intramolecular manifestation of the wave nature of matter. At least this will serve as an illustration on which to make the preceding ideas more precise. The band in question extends from λ2476 to λ2482 and is found only in emission. It has a sort of head at λ2476 and is accompanied by a weaker band with a head at λ2469 but this one does not show the banded structure. To discuss these as nuclear diffraction bands we will suppose that the head at 2476 corresponds to the transition from the zero vibration state of curve I (Fig. 5) to zero nuclear energy on curve II which will for simplicity be supposed to be absolutely horizontal under the minimum of curve I. On this view curve II is probably that of the ground state of the Hg_2 molecule and curve I one for which the molecule separates into one Hg atom in its normal state and one in the $^3P_2$ state, which is upper state for the forbidden atomic line λ2270—but these points are not essential to the present discussion.

The band whose head is at λ2469 may be supposed to represent transitions into the continuous range above II from the first vibrational level of curve I. This fixes the vibration frequency in curve I at 106.2 cm^{-1} and therefore the constant, a, giving the breadth of the wave function,

$$a=8.2/(\omega\mu)^{1/2}=0.08$$

where a is in Angstrom units, $\omega=106.2$ and μ is half the atomic weight of Hg. This formula is a convenient way of writing the general formulas

$$a^2=h/2\pi(\kappa\mu)^{1/2} \text{ and } \nu=(\kappa/\mu)^{1/2}/2\pi, \quad (C.G.S. \text{ units}),$$

from the wave mechanics of the harmonic oscillator.

On the horizontal part of II the function ψ_{II} will have the form

$$\psi_{II}=\lambda \sin 2\pi(x/\lambda+\delta)$$

in which λ is the de Broglie wave-length, h/p, given by the convenient formula,

$$\lambda(A.U.)=25.7/(\mu\nu)^{1/2}$$

where ν is the energy of the state in cm^{-1} reckoned up from the horizontal part of II. The factor λ, in front, comes from the normalization of the wave

[13] Rayleigh Proc. Roy. Soc. A119, 349 (1928), especially p. 353.

functions for the continuous. As explained before δ, as well as λ, depends on ν. Assuming complete non-polarity for simplicity, the intensity of transition from state I to a level ν cm^{-1} up from the horizontal part of II is therefore proportional to the square of,

$$I_0(\nu) = \int e^{-x^2/2a^2} \cdot \lambda \sin 2\pi(x/\lambda + \delta) dx$$

$$= (2\pi)^{1/2} a\lambda \sin 2\pi\delta \cdot e^{-2\pi^2 a^2/\lambda^2}.$$

The factor with the exponential function represents the effect of the uncertainty principle, the sine factor gives the banded diffraction structure. Inserting the numerical value of a and the relation of λ to ν the exponential factor becomes $e^{-\nu^2/52.3}$, so that the intensity for $\nu = 100$ cm^{-1} will be about $e^{-4} = 2$ percent of the value for $\nu = 0$. The Rayleigh band is about 90 cm^{-1} in extent so that the order of magnitude agreement is a good one. But it does not appear to show such an exponential intensity decay.

Next we have to consider roughly the spacing of the diffraction maxima in the spectrum. A rough approximation is to suppose that curve II is simply L-shaped, that is, it extends horizontally a distance d to the left of the minimum of I and then turns up abruptly to infinity. For a range of ν of only $0-100$ cm^{-1} this is not as bad an approximation as it might at first seem. At any rate for such a curve ψ_{II} has a node at the place of infinite slope and so δ is simply given by

$$\delta = d/\lambda = d\nu^{1/2}/2.57$$

and the maxima come at $\delta(\nu) = (n + \frac{1}{2})$ with n an integer. This simple argument would then put the nth maximum at

$$\nu^{1/2} = 2.57(n + \tfrac{1}{2})/d$$

This would make the maxima close together at the short-wave side and be more widely spaced toward the long-wave side. Not only is this true but $\Delta\nu^{1/2}$ is fairly constant for Rayleigh's band as Table I based on his data shows.

TABLE I. *Values of $\Delta\nu^{1/2}$ for the Hg_2 bands observed by Rayleigh.*

Wave-number	ν	$\nu^{1/2}$	$\Delta\nu^{1/2}$
40372.3	0.0	0	
354.0	18.3	4.28	
350.6	21.7	4.66	0.38
346.8	25.5	5.06	0.40
342.6	29.7	5.45	0.39
337.9	34.4	5.87	0.42
332.4	39.9	6.32	0.45
326.1	46.2	6.80	0.48
320.3	52.0	7.22	0.42
313.5	58.8	7.67	0.45
306.7	65.6	8.10	0.43
298.7	73.6	8.58	0.48
291.7	80.6	8.98	0.40
284.4	87.9	9.38	0.40

From the experimental value of $\Delta\nu^{1/2}$ one infers that d is about 6.4A which is a rather large value. But this may well be a consequence of the over simplification of the curve *II*.

Another assumption for *II* is that it is given by a straight-line of small slope, its equation in the neighborhood of the minimum of *I* being

$$U(x) = -kx$$

For this one finds for the characteristic functions

$$\psi_{II}(W, x) = (x + W/k)^{1/2} J_{1/3}\left[\left(\frac{x + W/k}{b}\right)^{3/2}\right]$$

in which $J_{1/3}(z)$ is the ordinary Bessel function of order 1/3 and

$$b = 3.345/(u_1\mu)^{1/3}$$

Here u_1 is written for k when the unit of energy is cm^{-1} and of length 10^{-8} cm, and the unit of μ is 1/16 the mass of an oxygen atom. The values of z for which $|J_{1/3}(z)|$ is a maximum are roughly (by inspection from the tables in Watson's Bessel Functions):

$m =$	1	2	3	4	5
$z_m =$	0.92	4.36	7.54	10.70	13.84
$\Delta z_m =$		3.44	3.18	3.16	3.14

For larger values of m, the ordinal number of the maximum, the interval approaches π. For larger m it is therefore sufficient to look for maxima at

$$(\nu/u_1 b)^{3/2} = (m\pi - 1.89)$$

which gives the law $\Delta\nu^{3/2} = u_1\pi b$. This assumption therefore does not fit Rayleigh's data.

The structureless band at λ2469.7 has already been supposed to be due to the transition from the first vibration level of state *I* on to the continuum of *II*. It may be apparently structureless since the ψ_I function for one vibration unit has a wider range than has ψ_I for zero vibration which tends to blur the diffraction effect. But it is hard to convince oneself that one unit of vibration energy can make so much difference.

The fact that these bands were found only in emission is consistent with the view here presented although this of course, is easily explained on more usual views by saying that their final state is an excited state of the molecule.

In conclusion it should be said that the existence of such diffraction bands either in emission or absorption (if *I* is a lower state than *II*) but not in both is a rigorous conclusion from quantum mechanics. It is not unreasonable to suppose that Rayleigh's band is a case of this but the interpretation must as yet be provisional and subject to confirmation, perhaps by the empirical determination of curves *I* and *II* through sharp bands coming from their discrete vibration levels.

§5. Additional Applications to Band Systems

Since the extension of Franck's postulate to band systems was first made the necessary data for its application to several more band systems has accumulated. This section is devoted to remarks on its application to some new band systems.

As already mentioned[9] the outstanding discrepancy between theory and experiment in the case of the visible bands of iodine has been removed by correction of a blunder in the use of the experimental data.

The iodine spectrum presents an interesting feature which was not amenable to treatment in the original Franck method, namely the somewhat irregular fluctuation of intensity in Wood's long series of resonance doublets. Such fluctuations probably are to be interpreted as arising from diffraction effects akin to those which are the subject of §4, except that we are now dealing with transitions of which both initial and final states are in the region of discrete energy levels. The main resonance doublet series, it is now known[14], arises from transitions from the $n'=26$ state of the excited molecule to various vibration states of the molecule in the normal electronic state from $n''=0$ to $n''=27$. Along this series of 28 doublets there are great intensity variations, some of the doublets being quite missing. Lenz[15] showed how this behavior is possible from correspondence principle considerations. From the criterion of the overlapping of the wave functions it is easily seen from Fig. 3 that from $n'=26$ to $n''=0$ to 27 are allowed transitions. The exact intensity of any particular one, however, will depend on the integral of the product of the wave functions of the initial and final states as in §2. And as in §4 this will depend very much on the exact phase relation of the nodes and loops of the two wave functions in question. These finer diffraction effects probably give rise to the intensity fluctuations in the resonance doublet series.

While the principle of their explanation is therefore precisely fomulated, the exact prediction unfortunately calls for a very accurate knowledge of the wave functions. This is lacking since for these large vibration quantum numbers it is quite inacceptable to treat the molecule as a harmonic oscillator or any other model for which ψ functions are at present exactly known.

The band systems which have been recently analyzed and on which the theory has been tested include especially the β bands of nitric oxide,[16] and the blue-green bands of diatomic sodium.[17] The vibrational analysis only for several more band systems has been recently published. In all of these cases the types of intensity distribution are those which this theory explains but lacking analysis of rotational analysis one is unable to use them for detailed verification of the theory. In this class at present may be mentioned the many band systems of the copper halides studied by Ritschl,[18] the absorption and

[14] Chapter VI of National Research Council Report on Molecular Spectra in Gases.
[15] Lenz, Zeits. f. Physik 25, 299 (1924).
[16] Barton, Jenkins and Mulliken, Phys. Rev. 30, 175 (1927).
[17] Loomis and Wood, Phys. Rev. 32, 223 (1928).
[18] Ritschl, Zeits. f. Physik 42, 172 (1927).

fluorescence spectra of S_2, Se_2, Tl_2, studied by Rosen,[19] the absorption spectrum of iodine monochloride observed by Gibson and Ramsberger,[20] that of chlorine and bromine studied by Kuhn,[21] the ultra-violet system of iodine analyzed by Pringsheim and Rosen,[22] and others.

In a recent article Herzberg[23] has obtained nice measurements on the intensity distribution in the second positive group of nitrogen under different conditions of excitation, one of the systems discussed in the original paper.[2] His criticisms of the paper[2] are already covered by the explicit statement made on p. 1183 that the theory treats only of relative transition probabilities and not of distribution of the molecules in the different excited states. The latter naturally depends on the conditions of excitation and cannot come out of any theory which makes no mention of these.

§6. Electron Jumps and the Franck Postulate

It is natural to ask why the Franck postulate does not apply to electron transitions in atoms, that is, to questions of relative intensity of lines in atomic spectra. The classical mechanical basis for the postulate consisted in saying that the absorbed quanta and the electronic motions involved much smaller amounts of momentum than were necessary to excite the nuclear vibrations. Therefore the principle, which may be said to be one favoring as little discontinuity in the orbits as possible, should also apply to the electron orbits. This is true since one recalls that the momentum of a quantum of visible light is very small compared with the orbital momentum of electrons in the initial and final orbits concerned in the emission or absorption of such light. (Nowadays one remembers this best by recalling that the relation $p = h/\lambda$ holds equally for light and for electrons, together with the fact that λ for visible light is 10^4 times the size of an atom.)

The answer is that the postulate *is* valid to a certain extent for relative probability of electron transitions. For example, the reason why the transition $50_2 \rightarrow 1_1$ (Bohr notation) is so much less probable than a transition $2_2 \rightarrow 1_1$ in atomic hydrogen is simply because the wave functions do not overlap as much in the former case as in the latter. For atomic spectra the principle does not have so much interest as in molecular spectra, on the other hand, because here the wave-length of the electron is enough greater that the range of the Heisenberg uncertainty principle is so broad that in turn the predictions of Franck postulates become so blurred as to be of almost trivial interest. In principle, however, it is just as true for electrons as for nuclear motions.

Finally it may be said that it is in this direction that the connection of the Franck postulate with the correspondence principle is to be found, although

[19] Rosen, Zeits. f. Physik **43**, 69 (1927).
[20] Gibson and Ramsberger, Phys. Rev. **30**, 598 (1927).
[21] Kuhn, Zeits. f. Physik **39**, 77 (1926);
Halban and Siedentopf, Zeits. f. Physik. Chem. **103**, 71 (1922).
[22] Pringsheim and Rosen, Zeits. f. Physik **50**, 1 (1928).
[23] Herzberg, Zeits. f. Physik **49**, 761 (1928).

this point today has only historical interest. The transition probabilities are related to the Franck postulate in the way here outlined and also are known to have the appropriate asymptotic connection with the Fourier coefficients of the classical motion which is demanded for the Bohr theory.[24]

In conclusion I should like to say that this paper is an outgrowth of work[3] done while abroad on a National Research fellowship and that it is a pleasure here to express my profound indebtedness to the fellowship board for its generous support of my studies.

PALMER PHYSICAL LABORATORY,
PRINCETON UNIVERSITY.
September 10, 1928.

[24] This fact is built into the very structure of wave mechanics and has been clearly worked out in the special case of the hydrogen atom by Eckart, Zeits. f. Physik **48**, 285 (1928).

NEW FEATURES OF THE RED BAND SYSTEM OF SODIUM

By F. W. Loomis and S. W. Nile, Jr.

Abstract

The occurrence of an infra-red edge to the red band system of Na_2 is reported and is explained in terms of the Franck-Condon theory of intensity distribution when account is taken of the shape of the potential energy curves as dissociation is approached. The same theory explains a head of the red system in the yellow-green, the reappearance of the orange "cathode-ray fluorescence" series in the infra-red, and the observed asymmetry in the two branches of the Condon "parabola."

IN ORDER to decide a point[1] concerning the lower level vibrational terms in the red band system of Na_2 the writers have used neocyanine plates to follow this system out into the infra-red where the bands with high values of n'' occur. It was there found that the system, instead of extending indefinitely towards longer wave-lengths, as is usual, actually terminates in a fairly sharp edge at 8150A = 12300 cm^{-1}, beyond which absorption ceases altogether. The whole situation, and in particular the contrast between the behaviors of the red and green systems is apparent in Figs. 1, 2 and 3.

Fig. 1 shows the visible absorption spectrum of sodium at various temperatures as taken with a dicyanine plate in a small glass Hilger constant deviation spectrograph. It can be seen that at low temperatures (lowest spectrum) only a few bands appear, near the origin of each system. As the temperature is raised the bands spread out, more or less symmetrically, on each side of the origins, partly because the increased density of molecules brings out the fainter bands, and partly because the increased temperature produces more molecules with high vibrational quantum numbers (n'').

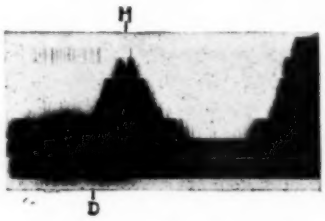

Fig. 1.

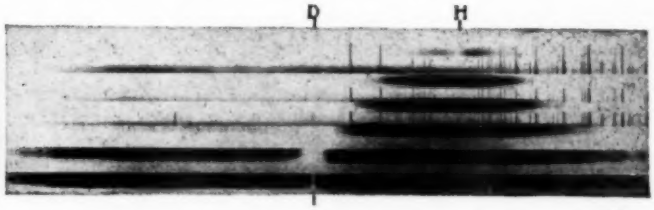

Fig. 2.

Fig. 1. Visible absorption spectrum of sodium vapor. Temperature and density increasing upward. *D* indicates *D* lines; *H* the green head of the red system. Comparison spectrum neon.

Fig. 2. Same as Fig. 1 but taken with a larger spectrograph on a panchromatic plate. Comparison spectrum iron.

Fig. 2, taken with a panchromatic plate in a larger spectrograph, shows part of the same region as Fig. 1, in greater detail.

[1] Loomis, Phys. Rev. **31**, 328 (1928).

Fig. 3, on the same scale as Fig. 2, but taken with a neocyanine plate, shows the termination of the red system in the edge at 8150A. The lowest

Fig. 3. Taken with the same spectrograph as Fig. 2, but with a neocyanine plate. Temperature and density increasing downward. *E* indicates infra-red edge. Comparison spectrum neon.

three spectra, which show the edge, were taken through sodium vapor so extremely dense that the transmitted light was of a deep violet color.

This is not a convergence limit in the usual sense since there is no continuous absorption beyond it; and since it is in entirely the wrong location to

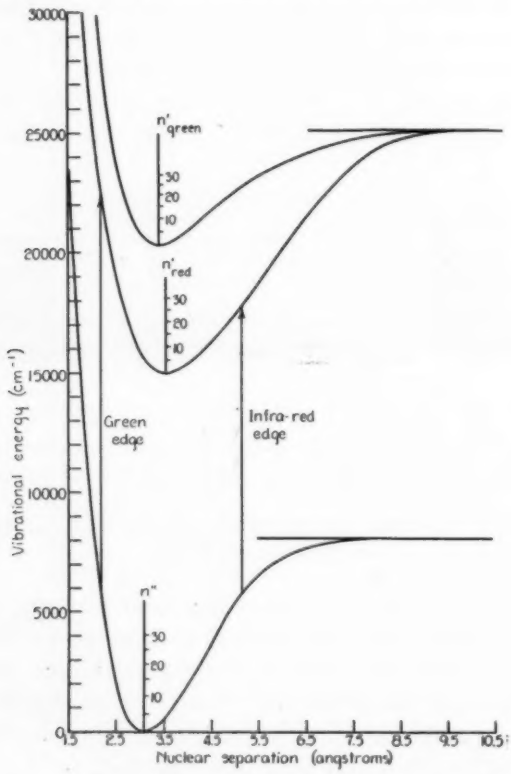

Fig. 4. Potential-energy functions of the three electronic levels.

correspond to a dissociation process. The explanation of this edge and, as it turns out, of other peculiarities of this band system is to be found in an un-

usual distribution of intensities of vibrational transitions which in turn can be deduced according to the procedure of Franck[2] and Condon[3] from an unusual relation between the potential-energy functions in the two electronic states.

The potential-energy curves for the two electronic states which take part in the red system, as well as for the upper electronic state of the green system, are shown in Fig. 4. For convenience the electronic energy is included as potential energy. The data from which the curves were calculated are given in Table I.

TABLE I. *Constants of the molecule in three electronic states.*

State of molecule:	Normal	Upper Green	Upper Red
Electronic term:	0	20301.70[1]	15006.68[5]
ω_0(cm^{-1}):	158.5[1]	124.13[1]	115.22[5]
$\omega_0 x$(cm^{-1}):	0.73[1]	0.84[1]	0.384[5]
D(volts)	1.0[1]	0.6[1]	1.25[1]
B_0(cm^{-1}):	0.1543[4]	0.1254[4]	0.1152
α(cm^{-1}):	0.00082[4]	0.00094[4]	0.00043
r_0(A):	3.08[4]	3.41[4]	3.56
U_2:	+4312	+2645	+2279
U_3:	−2680	−1736	−1040
U_4:	+ 642	+ 407	+ 192

Because of the lack of a reliable analysis of the rotational structure of the red bands, no measured values of B_0' and α' are available. Those in Table I were, however, estimated, probably with greater accuracy than is here needed, by making use of the empirical relations of Mecke[6] and Birge,[7] that B_0/ω_0 and $R=2xB_0/\alpha$ are approximately constant during a transition. In the green system $B_0''/\alpha''=0.00097$ and $B_0'/\alpha'=0.00101$. Hence a plausible guess for the red system is $B_0'/\alpha'=0.00100$, yielding $B_0'(\text{red})=0.1152$. In the green system $R''=1.73$ and $R'=1.81$. An estimated $R'=1.76$ for the red system leads to $\alpha'=0.00043$. u_2, u_3 and u_4 in Table I are the coefficients of the quadratic, cubic and biquadratic terms in $(r-r_0)$ in the expression for the potential energy, calculated by Condon's formulas.[3]

Now the Franck-Condon procedure for finding the most probable vibrational transitions is to assume that they correspond to the impact of a light quantum on a molecule in which the nuclei are at rest at one or the other extreme of a vibration, and that, owing to the large nuclear mass, the transition takes place without change of r and without setting the nuclei in motion. This means that each such transition is represented by a vertical line from a point on the lower to a point on the upper curve in Fig. 4. The initial and final vibrational quantum numbers can be obtained by projecting these points horizontally onto the scales of n' and n'' and *the frequency of the light*

[2] Franck, Trans. Faraday Soc. **21**, 438 (1926).
[3] Condon, Phys. Rev. **28**, 1182–1201 (1926).
[4] Loomis and Wood, Phys. Rev. **32**, 223 (1928).
[5] Fredrickson, Phys. Rev. **31**, 1130 (1928).
[6] Mecke, Zeits. f. Physik **32**, 823–834 (1925).
[7] Birge, not yet published.

absorbed in the process is represented by the length of the vertical line. It is usual to represent the results as a graph of the values of (n', n'') associated with the most probable transitions, but for our present purpose it is preferable to plot ν against n''; or better, since n'' is less accurately known than the corresponding vibrational energy T'', to plot ν against T''.

The resulting curves for the red and green systems, based on the potential-energy curves of Fig. 4, are shown in Fig. 5. It will be seen that the theoretical curve for the red system shows a minimum frequency at 12000 cm^{-1}, which undoubtedly corresponds to the observed absorption edge at 12300 cm^{-1}, with quite satisfactory accuracy for this type of computation.

The peculiarity in the relationship between the potential-energy curves of the two molecular states which results in the infra-red edge is essentially this: Although the normal molecule is more tightly bound than the excited one in the sense that the nuclei are closer together $(r_0'' < r_0')$ and the frequency of vibration is greater $(\omega_0'' > \omega_0')$, it is at the same time less tightly

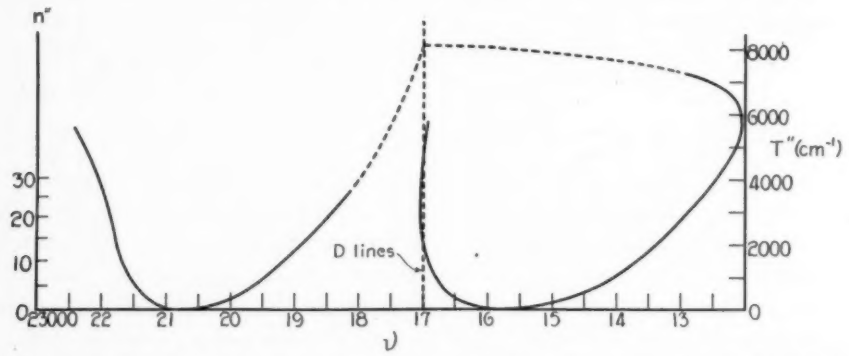

Fig. 5. Calculated locus of most probable vibrational transitions for each vibrational quantum state, n'' (scale at left) or for each amount of vibrational thermal energy, T'' (scale at right).

bound in the sense that the energy required to dissociate it is less $(D'' < D')$. This unusual relationship has as a consequence that the potential energy curve of the excited molecule is flatter near the minimum and also has its minimum further out than that of the normal level, but that it eventually rises higher. The result is that the frequency of the light absorbed during the transition, represented by the length of the vertical line joining the two potential-energy curves, at first decreases with increasing r, but that eventually it must increase again and that there is therefore a minimum at about the point where the vertical arrow is drawn in Fig. 4. It should be noted that while the location of this minimum frequency depends on the estimated constants of the upper state, its existence follows necessarily from the fact that $\omega_0'' > \omega_0'$ while $D'' < D'$.

Fig. 5 also affords an explanation of the curious appearance of the yellow-green region in the absorption spectrum of very dense sodium vapor. It can be seen in Fig. 1 that as the vapor density is raised the red system expands across the D lines and appears to come to a head at about 5500A = 18200

cm^{-1}, in a region of very strong absorption, which is indicated by H in Figs. 1 and 2. The region of just shorter wave-length than this is comparatively transparent, though not completely so. At still shorter wave-lengths the green system shows up strongly, so that there is a narrow transparent region which sometimes looks rather like an emission band. In Fig. 5 it appears that the curve of most probable transitions for the red system has a maximum frequency at 17000 cm^{-1}. This almost certainly corresponds to the observed head at 18200 cm^{-1}, the large error being due to the necessity of using the steep parts of the potential-energy curves in the calculation. The green system certainly extends across this region, to convergence at the D lines, but the bands which occur here are due to molecules with such high vibrational energy that they are rather rare at these temperatures, and the bands rather weak. Hence the comparative, but not complete, transparency just short of 5500A.

A further characteristic of the bands of the red system can be deduced from the character of the potential-energy curves, as follows: As is apparent in Fig. 4, the potential-energy curve of the normal molecule rises more rapidly at first than that of the excited molecule ($r_0'' < r_0'$ and $\omega_0'' > \omega_0'$) but does not have to rise so high ($D'' < D'$); hence it becomes sensibly horizontal at a much smaller value of r. For instance, according to Fig. 4 the lower level molecule is nearly dissociated at 6A, where the upper one has only about half the necessary energy. Hence the vibrational levels of the lower electronic level are here crowded closely together, while those of the upper electronic level are still well separated. Hence $\omega'' < \omega'$ in this region. Consequently, by Mecke's rule, $B'' < B'$ and the bands must degrade to the violet. That is, although the bands near the system origin are sharply degraded to the red, and have their heads on their R branches, very close to their origins, the heads must finally move away to infinity and eventually reappear on the other side, on the P branches.

This is a little surprising, because a simple calculation based on the constants of Table I, shows that as long as a linear representation of B as a function of n will suffice, the displacement of band heads from their origins is quite insignificant. Indeed this displacement, $\nu_0 - \nu_H = B'B''/(B' - B'')$, amounts to only 0.46 cm^{-1} at the origin of the system, and the variation of this quantity,

$$\delta(\nu_0 - \nu_H) = \left(\frac{B''}{B' - B''}\right)^2 \alpha' \delta n' - \left(\frac{B'}{B' - B''}\right)^2 \alpha'' \delta n''$$

would not in any case amount to more than a few tenths of a cm^{-1}. One is forced to conclude that the linear representation of B becomes *completely* inadequate as dissociation is approached.

It may well be that the changing structure of the bands as one proceeds towards the infra-red accounts for the discrepany reported by Frederickson,[5] between the absorption heads and the magnetic rotation lines. The magnetic rotation lines to which vibrational quantum numbers can be assigned coincide, according to theory,[1] with the R branch heads only, since Q branch lines

should not produce rotation. In the case of bands near the system origin, measurements of absorption heads will also be made at the head of the R branch, since this will be stronger than the head of the Q branch and will stand out at the edge of the band. But as one proceeds into the infra-red the appearance of the bands will change and the lines of the Q branch will pile up on each other so that it will be natural to measure them as the absorption head. In this case there will be a discrepancy between magnetic rotation and absorption measurements.

The series of bands in the orange found by Wood and Galt[8] in the cathode-ray fluorescence of sodium vapor has been interpreted by Schüler[9] as belonging to the red band system. The spacing between successive bands of this series is approximately that of the lower vibrational levels. Sodium molecules are presumably excited by collisions of the second kind with excited sodium atoms, which give the molecules 2.1 volts energy and leave them in the upper level of the red system and with a very limited range of values of n' and j'. These molecules then return to the various vibrational levels of the lower electronic level and in the process emit the series of bands, very much as in fluorescence. The occurrence of a few bands of higher frequency than that of the D lines is accounted for in the same way as anti-Stokes lines in fluorescence, by the molecules which happened to possess one or more vibrational quanta before they were excited. On this interpretation the series of bands in the orange, which was reported by Wood and Galt, correspond to transitions in which the molecule returns to a comparatively low value of n'', and they would be represented on the usual Franck-Condon diagram, by a horizontal row of points at the value of n' which the 2.1 volts happen to excite and *lying on, or near, the left arm of the Condon parabola.* It is expected however that transitions will also take place to much higher values of n'', corresponding to the right arm of the parabola; and indeed that the transitions to the right arm will be greatly preferred over those to the left arm, for a reason which will be discussed below. The results of the present paper make it clear that the wave-length of the bands corresponding to the right arm of the parabola in this cathode-ray series should be in the neighborhood of 8000A not far short of the infra-red edge. This was verified when the cathode-ray fluorescence was rephotographed with a neocyanine plate,[10] and it was found that the series actually do recur in this region.

A point which seemed to stand in the way of the above interpretation of the cathode-ray fluorescence spectrum has recently been cleared up in a discussion with Professor J. Franck. The difficulty was that Wood and Galt published a spectrum in which the series of cathode-ray fluorescence bands appear to be reversed. Now the processes which give rise to the cathode-ray fluorescence series may be symbolized by

$$A'+M(n_0'')=A+M(n')=A+M(n_1'')+h\nu$$

[8] Wood and Galt, Astrophys. J. **33**, 72–80 (1911).
[9] Schüler, Zeits. f. Physik **43**, 474–479 (1927).
[10] Wood and Loomis, not yet published.

which indicates that in the first stage an excited atom A' gives up its energy to a molecule in the normal electronic level with n_0'' vibrational quanta, thereby becoming a normal atom A and raising the molecule to the upper electronic level with n' vibrational quanta. In the second stage the molecule emits the quantum $h\nu$ and returns to the lower electronic state with an altered number n'' of vibrational quanta. If these processes were reversed in a single step, as the apparent reversal of the spectrum seems to indicate, it would imply that the quantum which was absorbed divided its energy between exciting an atom and adding a few vibrational quanta to a molecule. If the possibility of this sort of three-body collision between a quantum, an atom and a molecule is admitted, it becomes difficult to account for the absence of this series in absorption in ordinary sodium vapor. The correct explanation which, although complicated, seems to correspond to the experimental conditions under which the spectrum is found, is probably as follows. It occurs on the background of "white-light fluorescence" of sodium vapor. The white light excites a very broad (say 50A) atomic D line fluorescence. This very broad D line becomes reversed in travelling over to the field of view of the spectroscope. It there excites a fluorescence series in the red band system and in this series the pattern of the reversed D line is repeated at intervals of ω'' from the exciting D lines. In the resulting spectrum the broad emission lines merge into an apparently continuous background, on which the reversed center recurs at intervals and appears to be an absorption series.

It appears to be a general feature of the intensity distribution cases where the Condon parabola is as wide open as this, that the right arm of the parabola is in reality much stronger than the left. In other words it is much more probable that a molecule with a given high value of n' will revert to a high than to a low value of n''. This effect is masked in absorption by the opposing effect of the Boltzmann factor, so that the two arms of the parabola appear about equally strong. It is however very marked in fluorescence series. In a detailed study by one of us of all the sodium fluorescence series reported by Wood, it was found that in every case where the absorbing line belonged to a band on the left arm of the Condon parabola the fluorescence series extended over to the right arm; but in most cases where the absorbing line belonged to the right arm the fluorescence series did not extend back to the left arm. The same asymmetry in the transition probabilities corresponding to the two arms is clearly apparent in Wood's experiments with fluorescence excited in sodium vapor by light of varying frequency from a monochromator. The explanation of this asymmetry is, in terms of the Franck-Condon theory quite simple. When n' is high the amplitude of vibration is large and the vibration extends well up onto the lip, or flat part, of the potential-energy curve. The molecule then spends a greater proportional part of its time on this part of the curve, i.e., with nuclei far apart and is more likely to emit the quantum when in this state. Transitions made when the nuclei are most widely separated correspond to the right arm of the parabola, and this arm is therefore more prominent, particularly for large values of n'.

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INTERPRETATION OF THE ATMOSPHERIC ABSORPTION BANDS OF OXYGEN

By Robert S. Mulliken

Abstract

It is shown that the atmospheric oxygen absorption bands can be attributed to a $^3S \rightarrow {}^1S$ transition from the normal (^3S) to a metastable ^1S excited state of O_2. This accounts for all the strong lines, and explains missing lines, without conflict with existing theory. Certain very weak series such as the A' band are, however, not yet explained. Of the three rotational levels for each value of j_k in the ^3S normal state, the two for which $j = j_k \pm 1$ show only a very small separation, which increases slowly with j_k, while the third is separated from the other two by an interval of about 2 wave-numbers which does not change with j_k (cf. Fig. 2 and Table I). The ^3S and ^1S states involved in the atmospheric bands may perhaps be attributed both to the same electron configuration, in agreement with a suggestion made in a previous paper. If this is the case, it is likely that a metastable ^1D state derived from the same configuration also exists, and that infra-red atmospheric bands corresponding to the transition $^3S \rightarrow {}^1D$ should be found.

Introduction

ALTHOUGH the atmospheric absorption bands of O_2 have been much studied,[1] and although their obvious structure appears very simple (cf. Fig. 1), no satisfactory explanation of this structure has yet been given. Valuable progress has, however, been made by Mecke, Dieke and Babcock,

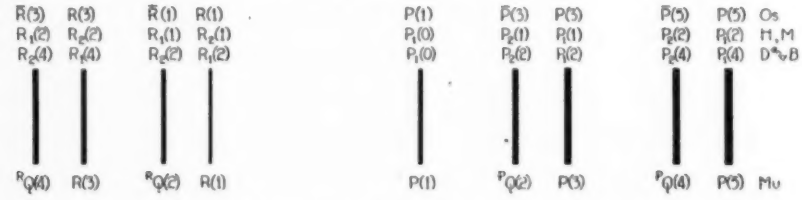

Fig. 1. *Arrangement and intensities of lines near center of A band. Comparison of notations of various investigators.* The lines are plotted on a frequency scale. The widths of the lines as drawn correspond to the widths or "intensities" of the lines as given by Dieke and Babcock. The designations of the lines are those given by various investigators (D. & B. = Dieke and Babcock, H. = Heurlinger, M. = Mecke, Os. = Ossenbrüggen, Mu = Mulliken). The line given above as $P_1(0)$ of D. & B. is really listed in their tables, evidently inadvertently, as $P_2(0)$.

and Ossenbrüggen. It is generally agreed that these bands form a progression with $n'' = 0$, and $n' = 0, 1, 2, 3, \cdots$, this conclusion being supported by combination relations between the bands.

For convenience in the following discussion, the arrangement and intensities of the central band lines in the A band ($n' = n'' = 0$) are shown in Fig. 1,

[1] R. Mecke, Phys. Zeits. **26**, 233 (1925); G. H. Dieke and H. D. Babcock, Proc. Nat. Acad. Sci. **13**, 670 (1927); W. Ossenbrüggen, Zeits. f. Physik **49**, 167 (1928); and a large number of earlier papers to which references may be found in the papers just cited.

together with the notation used by various investigators. In the present paper, a new notation is adopted for systematic reasons.

The following combination relations (re-expressed in the present notation) have been given by Mecke, and later by Dieke and Babcock:

$$R(j-1)-P(j+1)=\phi_1(j,n'') \tag{1}$$

$$^RQ(j)-{}^PQ(j)=\phi_2(j,n'') \tag{2}$$

Equations (1) and (2) mean that the differences of suitably chosen R and P, or ^RQ and ^PQ, lines are functions only of the quantum numbers of the lower electronic state, and are therefore the same for the entire series of atmospheric bands; this relation is demonstrated with great accuracy for the stronger bands by the data of Dieke and Babcock. Equation (1) is given also by Ossenbrüggen, who shows, furthermore, that the ultra-violet Schumann absorption bands of O_2 share $\phi_1(j, n'')$ with the atmospheric bands.

All these investigators interpret $\phi_1(j, n'')$ as a Δ_2F'', and all (except Ossenbrüggen) interpret $\phi_2(j, n'')$ as another Δ_2F'': $\phi_i(j)=\Delta_2F_i''(j)=F_i''(j+1)-F_i''(j-1)$, $i=1$ or 2. All agree with the assumption, first made by Mecke, that alternate lines are missing in each branch (as in most of the He_2 bands); this assumption is necessary to avoid the assumption of half integer jumps in the rotational quantum number.

Mecke, and Dieke and Babcock, interpret Eqs. (1) and (2) by means of the following assumed relations, involving a double set of rotational terms in both upper and lower electronic states:[2]

$$R(j)=F_1'(j+1)-F_1''(j) \tag{3}$$

$$^RQ(j+1)=F_2'(j+1)-F_2''(j) \tag{4}$$

$$P(j)=F_1'(j-1)-F_1''(j) \tag{5}$$

$$^PQ(j-1)=F_2'(j-1)-F_2''(j) \tag{6}$$

Granting the correctness of Eqs. (3)–(6), the terms $F_1'(j)$, $F_2'(j)$, $F_1''(j)$, $F_2''(j)$ can be completely determined to within additive constants. Results are given in the references cited.[1] But the correctness of these equations is not assured, since all the measured bands have $n''=0$, so that it is not possible to obtain combination relations for the upper electron level. A very serious objection to Eqs. (3)–(6) is the fact that—at least for a molecule which, like O_2, is homopolar—they would almost necessarily correspond to a $^2S\rightarrow{}^2S$ transition;[3,4] this, however, is impossible for neutral O_2, because the latter has an even number of electrons.

[2] The parameter j in the *right* hand sides of Eqs. (3)-(6) is not supposed to be *necessarily* identical with the true quantum number j. In the symbols $R(j)$, etc., on the *left* of the equation, however, j *is* the supposed true j corresponding to the present interpretation.

[3] The fact that only P-form and R-form branches are observed probably shows that $\Delta\sigma_s=0$, and probably also that $\sigma_s=0$ (if $\sigma_s>0$, weak Q-form branches would also be expected and would almost certainly have been observed). The alternate missing lines show *definitely* that $\sigma_s=0$, since otherwise, as e.g. in a $^1P\rightarrow{}^1P$ transition, alternate lines would at most be displaced, but not missing. Hence it is practically certain that the transition is $S\rightarrow S$. If Eqs.

Supposing Eqs. (3)–(6) to be correct, we should have for the doublet separations in the R and P branches,

$$\begin{aligned} {}^{R}Q(j+1)-R(j)=D_R(j)&=[F_2'(j+1)-F_1'(j+1)]-[F_2''(j)-F_1''(j)] \\ &=D_R'(j+1)-D_R''(j) \end{aligned} \tag{7}$$

$$\begin{aligned} {}^{P}Q(j-1)-P(j)=D_P(j)&=[F_2'(j-1)-F_1'(j-1)]-[F_2''(j)-F_1''(j)] \\ &=D_P'(j-1)-D_P''(j) \end{aligned} \tag{8}$$

The quantities $D_R''(j)$ and $D_P''(j)$ should be the same for all the bands,[4a] since $n''=0$ for all, but $D_R'(j)$ and $D_P'(j)$, and therefore $D_R(j)$ and $D_P(j)$, would be expected to depend at least slightly on n', which differs from band to band. But it is found experimentally (as the reader can verify from the data of Dieke and Babcock) that $D_R(j)$ and $D_P(j)$ are with great accuracy the same for all the bands, that is, *independent* of n'. This suggests that, contrary to Eqs. (3)–(6), $D_R'(j)\equiv 0$ and $D_P'(j)\equiv 0$, i.e., that the rotational levels of the upper electron state are truly single.[4] If this is the case, it becomes necessary to suppose at the same time, in order to account for the observed fact that corresponding doublet widths $D_R(j)$ and $D_P(j)$ are slightly different, that the final levels are at least triple.[4a]

The fact that $D_R(j)$ and $D_P(j)$ are both independent of n' can be stated in another way by saying that the following combination relations, in addition to those expressed by Eqs. (1)–(2), hold with an accuracy as great as the latter.

$${}^{R}Q(j)-P(j+1)=\phi_{21}(j,n'') \tag{9}$$

$$R(j-1)-{}^{P}Q(j)=\phi_{12}(j,n'') \tag{10}$$

New Interpretation of Atmospheric Bands

We know definitely from Ossenbrüggen's work that the lower electron level of the atmospheric bands is identical with that of the ultra-violet (Schumann) bands, and therefore that it is an S level, since the Schumann bands consist of P-form and R-form branches only, corresponding to an $S\rightarrow S$, in all probability a ${}^3S\rightarrow{}^3S$ transition.[5] The rotational levels should then be triple for the lower electronic state of the atmospheric bands. Also, the upper electronic state of the atmospheric bands must almost certainly be an S state.[3]

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(3)-(6) are correct, it must almost certainly be ${}^2S\rightarrow{}^2S$; ${}^3S\rightarrow{}^3S$ in which two of the three levels of each triplet are accidentally coalescent would also be a remote possibility.

[4] Another indication that Eqs. (3)-(6)—cf. Fig. 1 for key to earlier designations—are incorrect is the fact that they give doublets of almost exactly similar type for the upper and lower rotational states; i.e. for both F_1' and F_1'' the effective quantum numbers T are almost exactly half integral, while for both F_2' and F_2'', the T values fall approximately 0.05 units below half integers. Such very close similarities between two different electronic states would be surprising.

[4a] If Eqs. (3)-(6) are accepted, $D_R''(j)\equiv D_P''(j)$; also $D_R'(j)\equiv D_P'(j)$. Separate designations D_R'' and D_P'' are used here because, in the new interpretation given below, the corresponding quantities are *not* identical: cf Eqs. (16)-(17).

[5] Cf. R. S. Mulliken, Phys. Rev. **32**, 213 (1928).

Eqs. (1)–(2) and (9)–(10) can be simultaneously satisfied, and the objections which apply to Eqs. (3)–(6) can be avoided, by assuming that the following Eqs. (11)–(14) hold instead of (3)–(6). It should be noted that Eqs. (11) and (13) are formally identical with Eqs. (3) and (5); only (12) and (14) involve essential changes. The formal relations expressed by Eqs. (11), (12), and (13) have also been assumed by Ossenbrüggen.

$$R(j)=F'(j+1)-F_2''(j) \tag{11}$$

$$^RQ(j)=F'(j)-F_1''(j) \tag{12}$$

$$P(j)=F'(j-1)-F_2''(j) \tag{13}$$

$$^PQ(j)=F'(j)-F_3''(j) \tag{14}$$

Eqs. (11)–(14) correspond to a ^1S upper electron level, and a ^3S lower level with the respective designations F_1, F_2 and F_3 for the rotational levels according as $j=j_k+1$, j_k, or j_k-1; these designations correspond to the system of notation recently proposed by the writer.[6] Levels $F_1(j+1)$, $F_2(j)$, and

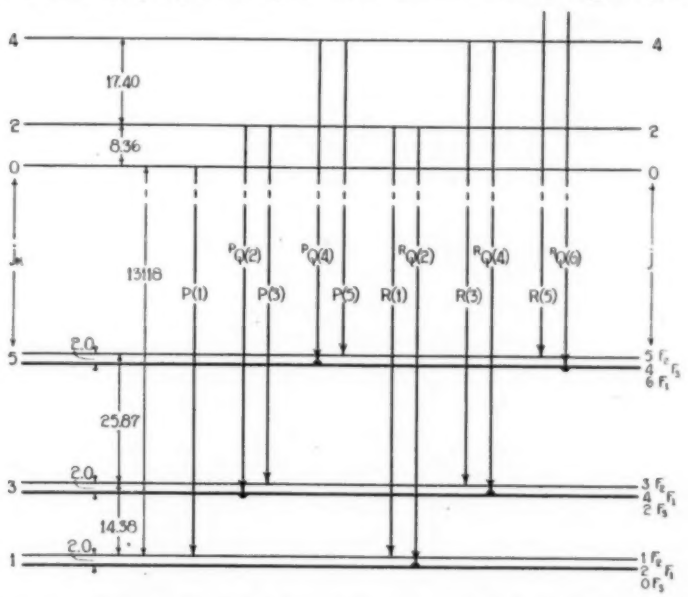

Fig. 2. *Lowest rotational levels of electronic states involved in atmospheric oxygen bands, and transitions corresponding to lines shown in Fig. 1.* The spacings of the levels (in wavenumbers) are given in the figure, except for the small intervals F_3-F_1 in the ^3S levels. The latter are not large enough to show with the scale used (cf. Table I for data). Note that the *sign* of F_3-F_1 reverses at $j_k=5$.

$F_3(j-1)$, for a given value of j, should form a close triplet, since the rotational energy is mainly given by $Bj_k(j_k+1)$; hence $R(j)$ and $^RQ(j+1)$, $P(j)$ and $^PQ(j-1)$, form the observed doublets.

The four observed branches are completely accounted for by Eqs. (11)–(14), if the rotational levels corresponding to $j=0, 2, 4, \cdots$ are present in

[6] R. S. Mulliken, Phys Rev. **30**, 144, 788 (1927).

the upper state, and, as in the Schumann bands, those corresponding to $j_k = 1, 3, 5, \cdots$ in the lower state. The way in which Eqs. (11)–(14) account for the observed relations can best be seen from Fig. 2. As can be seen from this figure, the four observed branches are the only branches which are possible, with the selection rule $\Delta j = 0, \pm 1$, for a $^1S \rightarrow {}^3S$ combination in a homopolar molecule composed of atoms with no nuclear spin.[7,7a]

Intensity relations. A characteristic feature of the atmospheric bands is the absence of one component in the first doublet of the P branch. This is now accounted for by the fact that the missing line in question, which would be $^PQ(0)$, is ruled out by the special prohibition of the transition $0 \rightarrow 0$ for j.[8]

The approximately equal intensity of the P and R branches is as expected for an $S \rightarrow S$ transition. No detailed explanation of other intensity relations can be given, however, since the intensity theory has not been developed for inter-system transitions, and since the intensity relations may be greatly distorted by the strong absorption. A few remarks based on the observed relations can, however, be made. In each doublet, one component has $\Delta j = \pm 1 = \Delta j_k$, the other has $\Delta j = 0 \neq \Delta j_k$.[7a] In a $^3S \rightarrow {}^3S$ transition, lines with $\Delta j \neq \Delta j_k$ would be very weak, but here this rule evidently does not apply, since the components with $\Delta j = 0$ are of about the same strength as the other components.[10] At the beginning of each branch there is, however, a decided inequality of intensity of the components of each doublet, in such a way that the component for which the mean value of j, i.e., $(j'+j'')/2$, is larger, is the more intense. In agreement with this formulation, the inequalities gradually disappear as j increases. This situation is at least superficially similar to that which exists in the doublets of $^2S \rightarrow {}^2S$ transitions.[9]

Isolation of rotational terms. From Eqs. (11)–(14) we have:

$$R(j-1) - P(j+1) = F_2''(j+1) - F_2''(j-1) = \Delta_2 F_2''(j) \tag{15}$$

$$D_R(j) = {}^RQ(j+1) - R(j) = F_2''(j) - F_1''(j+1) \tag{16}$$

$$D_P(j) = {}^PQ(j-1) - P(j) = F_2''(j) - F_3''(j-1) \tag{17}$$

$$R(j) - P(j) = F'(j+1) - F'(j-1) = \Delta_2 F'(j) \tag{18}$$

[7] If alternate rotational levels were not missing (characteristic of a homopolar molecule whose atoms have no nuclear spin—cf. W. Heisenberg, Zeits. f. Physik **41**, 239 (1927) and F. Hund, Zeits. f. Physik **42**, 106 (1927)), additional branches should be present.

[7a] The observed branches conform to the selection rule $\Delta j_k = \pm 1$, but it is possible that this is not significant, since it is an automatic consequence of the alternate missing levels and of the selection rule $\Delta j = 0, \pm 1$.

[8] The quantum numbers j_k, s and j in a case b molecular state like ^3S are completely analogous in the determination of intensity relations to l, s, and j in an atom.[9] The transitions from a ^1S molecular level with $j = 0$ to a ^3S molecular level with $j_k = 1$ are then entirely analogous to those from a ^1S to a ^3P atomic level, in which $^1S \rightarrow {}^3P_0$ is ruled out by the $0 \rightarrow 0$ prohibition, and only $^1S \rightarrow {}^3P_1$ occurs (e.g. Hg λ2537).

[9] Cf. e.g. the discussion of $S \rightarrow S$ transitions by the writer, Phys. Rev. **30**, 139 (1927).

[10] This result is rather unexpected, and conflicts with a probably not well-founded statement made earlier by the writer[4] to the effect that lines for which $\Delta j \neq \Delta j_k$ should be weak in $^3S \rightarrow {}^1S$ transitions as in other cases. Intersystem transitions apparently show exceptional behavior.

Except for notation, Eqs. (15) and (18) are just as consistent with Eqs. (3, 5) as with Eqs. (11, 13). Hence for $\Delta_2F'(j)$ and $\Delta_2F_2''(j)$ the results of Dieke and Babcock and Ossenbrüggen still hold.[11] Their formulas for $F'(j)$ and $F_2''(j)$, which can be determined in the usual manner from the Δ_2F's, also remain valid. These results are, $F'(j)=B'[j(j+1)]+\cdots$, $j=0, 2, 4, \cdots$, with $B'=1.392$ for $n'=0$; and $F_2''(j)=B''[j_k(j_k+1)]+\cdots$, $j_k(=j)=1, 3, 5, \cdots$, with $B''=1.438$. The effective rotational quantum numbers are almost accurately integral in both cases, i.e., only a very small linear term in j is needed in representing $F(j)$. If desired, the exact term values (except for an additive constant) can be built up by summation of Δ_2F's (cf. Fig. 2).

For the F_1'' and F_3'' levels, the Δ_2F'' expressions can be obtained by suitable combination of the quantities in Eqs. (15) and (16) or (17). Using the data of Dieke and Babcock, it is found that the expressions $\Delta_2F_1''(j_k)$, $\Delta_2F_2''(j_k)$, and $\Delta_2F_3''(j_k)$ are almost identical, i.e. B'' is practically the same for all three, and the effective rotational quantum numbers differ only very slightly for the three levels.[12] As shown by the application of Eqs. (16) and

TABLE I. *Spacings of triplets in rotational levels of* ^3S *state.*

$j(=j_k)$	$D_P(j)=F_2(j)-F_3(j-1)$	$D_R(j)=F_2(j)-F_1(j+1)$	Average	$j(=j_k)$	F_2-F_3	F_2-F_1	Average
1		1.88		15	1.86	2.31*	*
3	2.09	1.94	2.015	17	1.87	2.29*	*
5	1.99	2.01	2.000	19	1.86	2.13*	*
7	1.94	2.01	1.975	21	1.82*	2.13*	*
9	1.92	2.07	1.995	23	1.81	2.19	2.00
11	1.90	2.09	1.995	25	1.80	2.19*	*
13	1.88	2.15	2.015	27	1.77	2.21*	*

Notes. The above values of $D_P(j)$ and $D_R(j)$ are the doublet separations in the P and R branches, respectively, according to the data of Dieke and Babcock, for the A band. (Better values could be obtained by using average values obtained from the whole series of bands, but the above data are sufficient to show the trend of affairs.) The meaning of the numerical values of j and j_k will be clear from Eqs. (16) and (17) together with the fact that $j_k=j$ for F_2 levels, $j_k=j+1$ for F_3 levels, and $j_k=j-1$ for F_1 levels. From the data given, it will be seen that F_3-F_1 is negative for the smallest values of j_k, but soon becomes positive and then increases slowly with j_k, remaining, however, in the observed range, always much smaller than the constant interval of 2.0 between F_2 and the average of F_1 and F_3.

(17), there is, however, an approximately constant difference of about 2 wave numbers between $F_2(j_k)$ and $[F_1(j_k)+F_3(j_k)]/2$. F_1 and F_3 themselves form a very narrow doublet whose size changes slowly with j_k; also, $F_3(j_k)-F_1(j_k)$ changes sign at about $j_k=5$. The relationships of the F_1'', F_2'', and F_3'' levels are best appreciated by a study of the doublet separations $D_R(j)$ and $D_P(j)$ of Eqs. (16) and (17) as shown in Table I and Fig. 2.

[11] Thus $\Delta_2F'(j)$ of Eq. (18) is the same as Dieke and Babcock's $F_1'(j+1)-F_1'(j-1)$, and $\Delta_2F_2''(j)$ of Eq. (15) is the same as Dieke and Babcock's $F_1''(j+1)-F_1''(j-1)$.

[12] These conclusions differ greatly from those of Mecke and Dieke and Babcock, according to whom[3] one set (their F_1) of F' and of F'' levels had effective quantum numbers almost exactly integral, another (their F_2) had effective quantum numbers departing considerably from integers (cf. ref. 4).

Difficulties. In the writer's opinion, the above interpretation of the atmospheric bands is the only one yet given which accounts for all the observed features of the strong band lines without obvious conflict with existing theory. It has, however, some weaknesses. First of all (in common with all earlier interpretations) it lacks the support of combination relations for the initial electronic states. These can be obtained only by new experimental work on the absorption of hot oxygen, so as to get detectable absorption from molecules with $n'' > 0$; this will be very difficult, because of the extremely low coefficients of absorption, requiring high pressure and long gas columns.

Another feature of the present interpretation which might give rise to doubts as to its validity is the peculiar spacing of the triplets in the ^3S levels (cf. Fig. 2 and Table I). This, however, does not appear to the writer to be a serious objection, for the following reasons. A consideration of the dissociation of a ^3S O_2 molecule into two atoms indicates that the molecules in F_2 states should give atomic states slightly different from those given by molecules in F_1 and F_3 states; e.g. perhaps the F_1 and F_3 levels both go over into $O(^3P_2)+O(^3P_2)$, while the F_2 levels go over into $O(^3P_2)+O(^3P_1)$. If an energy separation corresponding to $^3P_1-{}^3P_2$ (about 150 wave-numbers) exists in the dissociated molecule, one may reasonably expect a corresponding separation to persist to some extent in the united molecule. These considerations indicate that the interval of 2 wave-numbers, independent of j_k, which separates the F_2 from the average of the F_1 and F_3 levels, is not in contradiction with a ^3S classification. The much smaller interval F_3-F_1, increasing with j_k, may reasonably be attributed in the usual manner to the interaction of the spin with the magnetic field developed by the molecular rotation.

Perhaps the most serious objection to the present interpretation is that the energy levels of Fig. 2 cannot be made to account for the various faint absorption lines which are present in the atmospheric bands in addition to the strong lines. Thus in the (0, 0) band (A band) there is a very faint series of doublets (A' band) comprising the lines of a P' and an R' branch whose members alternate with the strong P and R doublets. If these alternate weak doublets were spaced symmetrically between the strong doublets, they could be interpreted as being the alternate missing lines of the strong series. These might perhaps after all be expected in very low intensity, corresponding to some small interaction neglected in the ordinary theory, even in a homopolar molecule without nuclear spin. But they are not symmetrically spaced, so that the suggested explanation seems improbable, since there is no evident reason why the alternate energy levels should be systematically perturbed.

It might be argued that the A' band is entirely independent of the A band, but if so, it is very difficult to understand why its lines have so nearly the same arrangement and spacing as the lines of the A band (cf. especially Ossenbrüggen's discussion).[1] It therefore seems probable that the present interpretation will need to be modified to account for the A' lines simultaneously with the A lines. Nevertheless, especially in view of the fact that

the A' lines are exceedingly weak as compared with the A lines,[13] it seems reasonable to regard the present interpretation as at least a probable first approximation to the complete explanation. It should also be remarked that the present is no worse than earlier interpretations in its inability to explain the A' lines.

BEARING OF RESULTS ON ELECTRONIC LEVELS OF THE OXYGEN MOLECULE

The writer has suggested elsewhere[5] that the normal, ^3S, state of O_2 is the lowest of the three states, ^3S, ^1D, and ^1S which are to be expected from an electron configuration $(1s^s)^2\ (2s^p)^2\ (2s^s)^2\ (3s^p)^2\ (2p^p)^4\ (3s^s)^2\ (3p^p)^2$. According to this suggestion, the ^1D and ^1S states should be metastable excited states lying within a few volts of the normal state. The reason for predicting metastability for the ^1D and ^1S states is similar to that for the expected ^1D and ^1S states of the O atom which have the same configuration as the normal, ^3P, state of the latter.

The ^1S upper level of the atmospheric bands seems to meet the specifications just given. It lies 1.62 volts above the ^3S level, with which it combines exceedingly weakly: the entire thickness of the earth's atmosphere gives only a moderate absorption for the transition $^3S \rightarrow {}^1S$, while for ordinary laboratory thicknesses, air is practically completely transparent. The fact that $^3S \rightarrow {}^1S$ corresponds to an inter-system combination tends of course to make the absorption coefficient low, but this fact alone is altogether inadequate to account for the actual *very* low coefficient.[14] Hence it appears that the ^1S state may rightly be classed as metastable. The interval of 1.62 volts between ^3S and ^1S is a reasonable one on the hypothesis that these states have the same electron configuration. It may for example be compared with the interval of 1.63 volts between 3^3P and 3^1P of the Mg atom, or with that of 0.8 volts between 2^3S and 2^1S of the He atom.

If this interpretation of the low ^3S and ^1S levels of O_2 is correct, one may predict the existence of a metastable ^1D level probably lying between them. Correspondingly, there should probably be infra-red atmospheric absorption bands associated with a weak transition $^3S \rightarrow {}^1D$.

According to the interpretation given above, there would be a considerable analogy between the emission transition $^1S \rightarrow {}^3S$ in O_2 (observed, absorption $^3S \rightarrow {}^1S$) and the emission of the green aurora line, which corresponds according to Sommer[15] to the transition $^1S \rightarrow {}^3P$ in the neutral oxygen atom.

WASHINGTON SQUARE COLLEGE,
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August 25, 1928.

[13] Although many of the A lines appear as very broad absorption lines in the solar spectrum, the corresponding A' lines are so narrow as to be difficult to detect (cf. e.g. Dieke and Babcock[1]). This indicates an *enormously* greater absorption probability for frequencies corresponding to the centers of A lines than for A' lines.

[14] Thus in the case of CO, the combination $^1S \rightarrow {}^3P$ occurs in absorption with sufficient intensity to be readily studied in moderate thicknesses of gas at atmospheric pressure or less, and the same bands (Cameron bands) are also observed in emission; cf. Birge, Phys. Rev. **28**, 1157 (1926) for references.

[15] L. A. Sommer, Naturwiss, **16**, 219 (1928). Cf. also the nebulium lines: cf. W. Grotrian, Naturwiss. **16**, 177 and 193 (1928) for review.

THE INFRA-RED ABSORPTION SPECTRA OF THE METHYL HALIDES

By Willard H. Bennett and Charles F. Meyer

Abstract

The molecules are symmetrical tops having one low moment of inertia. Two types of bands are expected, one arising from vibration parallel to the axis of symmetry, $\parallel$ bands, and the other from vibration perpendicular to the axis of symmetry, $\perp$ bands; the appearance of each type is described. There are seven bands for each of the four compounds. The twenty-eight bands fall into seven series, A to G inclusive. Two of the four bands of series A lie beyond the range of observation. Series A, C, E and F are made up of bands of the $\parallel$ type, and series B, D, and G, of bands of the $\perp$ type. The series converge towards the known bands of methane with decrease in the atomic weight of the halogen in the halide. The envelopes of the bands of the $\parallel$ type demonstrate the existence of P, Q, and R branches. The doublet separations for the various bands of the same compound appear to be the same; the chloride may however present an exception to this rule. In passing from compound to compound, the doublet separations increase with decrease in the atomic weight of the halogen in the halide. The band of series A for methyl fluoride has been resolved, and it is revealed that the P and R branches consist of a single series of lines. Strong convergence in the spacing is present. The bands of the $\perp$ type have all been resolved. Every third line is more intense than the others. The spacing converges in series B toward lower frequencies, and in series D and G toward higher frequencies. The mean frequency intervals from band to band of the same compound are found to vary markedly. The explanation of this variation presents a theoretical problem of interest.

Introduction

RECENT improvements in the apparatus available for measuring infra-red absorption have made possible the detailed study of spectra of much greater complexity than could be observed only a few years ago. As a consequence, the spectra of polyatomic molecules containing more than one heavy atom have become subject to investigation. Theoretical considerations led to the belief that the vibration rotation spectra of the methyl halides, CH_3F, CH_3Cl, CH_3Br, CH_3I, in the gaseous state, offered a promising field for study.

Stereochemical evidence indicates that the molecules consist of a carbon atom lying within a tetrahedron, with the three hydrogen atoms and the halogen atom at the four corners. The supposed form of the molecule is represented in perspective in Fig. 1, the carbon atom being denoted by C, the three hydrogens by H, and the halogen which varies from compound to compound by Z. The carbon atom and the halogen determine an axis about which the hydrogen atoms are symmetrically placed. The center of gravity of the molecule probably lies between the carbon and the halogen. The principal axes of inertia lie along the lines marked X, Y, and Z, and the moments of inertia about these axes will be referred to as A, B, and C respectively. In the XY-plane the three axes which lie above the lines joining the hydrogen atoms

to the carbon are physically indistinguishable from each other, and consequently the moments of inertia about these axes will all be equal. From this it follows that the ellipsoid of inertia for this type of molecule degenerates into a spheroid and the moments of inertia about all axes in the XY-plane which pass through the Z-axis must be the same, therefore $A=B$. Moreover, if the distance of the halogen from the carbon were about the same as the distance of the hydrogens from the carbon then $A(=B)$ would be much greater than C, for the magnitude of the former would be determined principally by the masses of the relatively heavy carbon and halogen atoms, and the magnitude of the latter would be determined by the light hydrogen atoms.

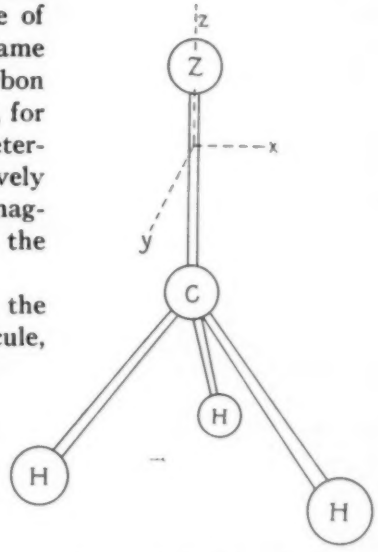

Fig. 1. Model of methyl halide molecule.

The Z-axis is the only unique axis and the permanent electric moment of the molecule, which must in general be assumed to exist, consequently lies along this axis.[1] Considerations based upon an extension of the vibrations of the ammonia molecule[2] show that the normal modes of vibration of the methyl halides consist of two types. In the first type the electric moment, and hence the change of electric moment vibrates parallel to the axis of symmetry. A band arising from such a vibration will be referred to as a "$\parallel$ band," and the fine structure to be associated with it will be briefly discussed.

Simultaneous rotation of the molecule about the Z-axis would not influence the absorption because the axes of vibration and rotation are coincident. But rotation about an axis in the XY-plane would influence the absorption. Simultaneous changes in the vibration state and the rotation state about such an axis will give rise to a series of absorption lines which are in first approximation equally spaced at a frequency interval $\Delta\nu=h/4\pi^2A$. These lines will form a P branch and an R branch which are schematically represented in Fig. 2a. In addi-

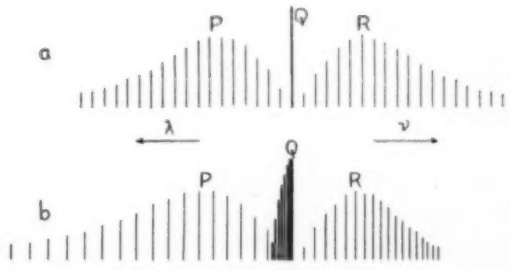

Fig. 2. Band of the $\parallel$ type.

[1] The remaining remarks of the introduction have as a basis the work of D. M. Dennison, Phys. Rev. **28**, 318 (1926); Reiche and Rademacher, Zeits. f. Physik **39**, 444 (1926); and Kronig and Rabi, Phys. Rev. **29**, 262 (1927), upon the rotation of molecules having the form of a symmetrical top.

[2] D. M. Dennison, Phil. Mag. **1**, 195 (1926).

tion there will be a Q branch of which the intensity will depend upon the ratio of the moments of inertia C/A. The smaller this ratio, the more nearly does the molecule resemble a diatomic one for which the ratio is zero and the Q branch is absent, as in the spectrum or hydrogen chloride.

Perturbations between the vibration and the rotation states will cause convergence in the positions of the lines in the P and R branches, these branches then presenting the appearance shown in Fig. 2b. Moreover the Q branch would have the modified appearance now indicated for it, consisting of closely spaced lines rapidly decreasing in intensity. The lines are so close that in the present state of technique there is no hope of separating them. When measurements are made upon a band of the type just described, and all conditions are favorable, the result is that of the upper curve of Fig. 5.[3] Under less favorable conditions the lines of the P and R branches are not separated by the spectrometer, and the band presents the appearance of the lower curve of Fig. 5, only the *envelopes* of all three branches being obtained.

In the second type of vibration referred to above, the atoms move in such a manner that the *change* of electric moment is a vector lying perpendicular to the axis of symmetry, and bands arising from such a vibration will be referred to as "$\perp$ bands." The fine structure is essentially more complex than for the $\parallel$ bands and may be described as follows: Simultaneous change in the state of the vibration along the X-axis and change in the state of rotation about the Y-axis only, would give rise to a band similar to the one already considered. But rotation about the Z-axis would no longer be without effect, since the Z-axis is now no longer parallel to the vibration of the electric moment, as in the $\parallel$ bands, but is perpendicular to it. Rotation about the Z-axis would cause the original band to be repeated at equal intervals to the right and to the left of the central position, with decreasing intensities. The separation between adjacent constituent bands would not be sufficient to separate them from each other entirely and they would overlap. In Fig. 3a such a group of constituent bands is shown, the individual members being placed higher or lower in the drawing so that they might be separately represented. Certain lines in the P and R branch near the center of each band will be missing. The separation between successive bands, expressed in frequency units will be $\Delta\nu = (h/4\pi^2)(1/C - 1/A)$ and since C is much smaller[4] than A this will be nearly equal to $h/4\pi^2C$. Inasmuch as the moment of inertia C is much smaller than A, the separation between the bands, while insufficient to prevent them from overlapping will still be much greater than the separation between the individual lines of the P and R branches. In Fig. 3b the overlapping bands are represented, and it will be seen that what one may hope to find is a series of Q branches, well separated, and about equally spaced. Between them will lie numerous closely packed lines in apparently confused

[3] The two faint lines appearing on the left slope of the Q branch are *not* lines of the Q branch, but are lines of the P branch which are superposed on the envelope of the Q branch.

[4] It should perhaps be emphasized that $C \ll A$ is not a general property of the symmetrical top molecule, but it happens to characterize the methyl halide group.

arrangement, which one could not hope to separate but they will form a background of absorption. The appearance of a region of absorption arising from vibrations of the electric moment perpendicular to the axis of figure of the molecule will then be that represented schematically in Fig. 3b, or as actually observed it may be seen in Fig. 6. The region as a whole will be spoken of as

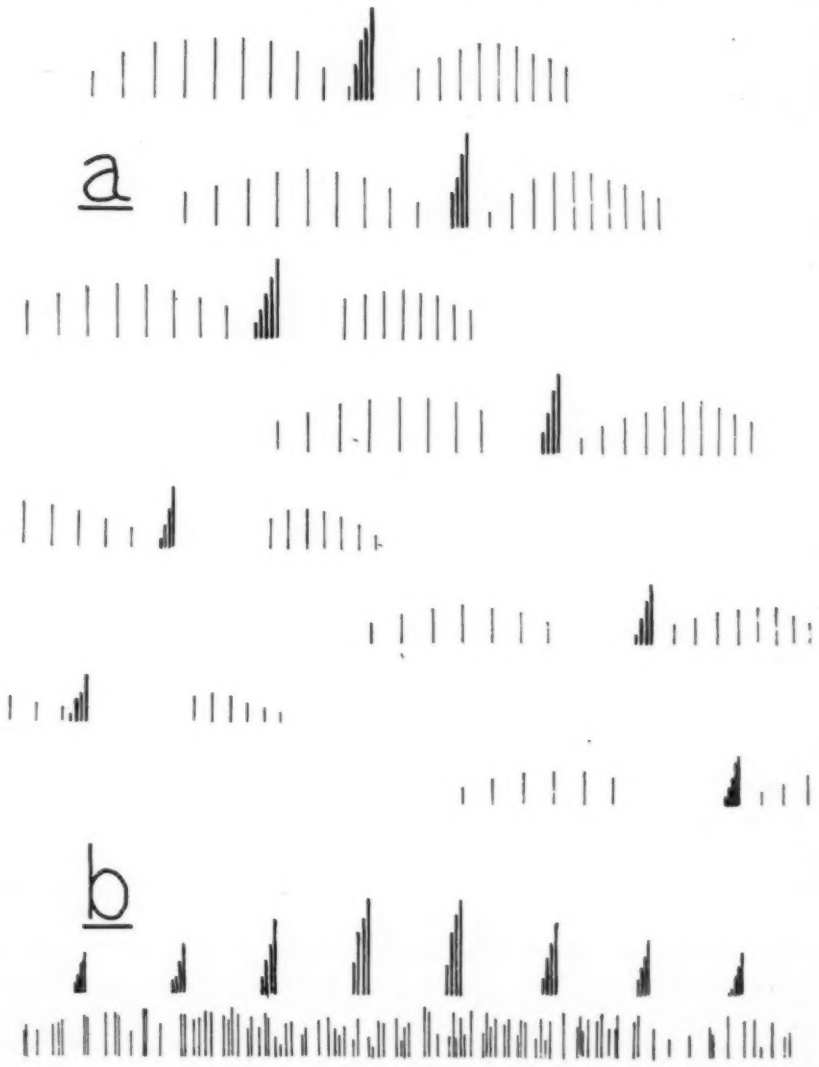

Fig. 3. Band of the ⊥ type.

a ⊥ band, and it will be noted that it consists of a single series of maxima which is most intense at the center of the band, being distinguished in this from bands of the ∥ type which consist of three branches as already explained.

In order that the maxima (succession of Q branches) should be well separated, the moment of inertia C must be small. The supposed smallness of

this moment of inertia in the methyl halides was an important factor in determining the choice of this group of molecules for investigation. An equally important factor was that because of the symmetry of position of the hydrogen atoms the ellipsoid of inertia degenerates into a spheroid and consequently the molecules belong to the type known as a symmetrical top.

Apparatus

A fore-prism spectrometer is used to select radiation of a fairly large range of wave-length from the emission of a Nernst glower. This is passed through the gas cell and focussed on the entrance slit of the grating spectrometer. A concave mirror of 20 cm diameter and 1 m focal length collimates the beam which is then incident upon the grating. The grating disperses the radiation, sending the first order beam back towards the concave mirror which now focusses the spectrum upon the exit slit of the spectrometer. This slit lets through the ultimate narrow range of wave-length of which the intensity is to be measured. A diagram of a similar spectrometer as well as details regarding the method of calculating wave-lengths have been given by a previous investigator of infra-red spectra.[5] In the present instrument a small concave mirror focusses the radiation on the junctions of a vacuum thermopile. Two thermopiles of the Pfund[6] type were used in the course of this investigation.

The thermopile is connected to a high sensitivity Leeds & Northrup galvanometer in a Moll-Burger thermo-relay.[7] A beam of light falling on the mirror of this galvanometer is reflected and thereupon focussed midway between the junctions of a thermo-element which is in turn connected to another high sensitivity galvanometer. Deflections of the secondary galvanometer are observed at a scale distance of seven meters. The resulting amplification is from one to two hundred depending upon adjustments. The relay was constructed by Professor Firestone.

The three Michigan echelette gratings which were used, were ruled under the supervision of Professor Barker. One with 7200 lines per inch (2834 lines per cm) ruled on a copper-nickel alloy was used in the 3μ region, one with 2880 lines per inch (1134 lines per cm) ruled on aluminum was used in the 7μ region, and one with 1440 lines per inch (567 lines per cm) ruled on a solder surface was used for all bands between 8μ and 15μ.

The absorption cell was built of brass. It was 6 cm long and was provided with rock-salt windows 5 mm thick. Side tubes with stop-cocks served for introducing and removing the gas. The cell was capable of holding a vacuum; the rise of pressure within the cell, after it had been evacuated, being about 0.1 mm in the course of two days. A pump, an ordinary manometer and a McLeod gauge served for controlling and measuring the pressure of gas used in each run. Pressures were known to within 1 mm for all runs.

[5] W. W. Sleator, Astrophys. J. **48**, 125 (1918).
[6] A. H. Pfund, Phys. Zeits. **13**, 870 (1912).
[7] W. J. H. Moll, and H. C. Burger, Phil. Mag. **50**, 624 (1925).

Sources of Material

Methyl chloride was obtained from the Dow Chemical Company in cylinders. An analysis furnished by the manufacturers indicated a sufficient degree of purity.

Methyl bromide (C.P.) was at first obtained from Kahlbaum, and later from the Eastman Kodak Company, in sealed glass bottles.

Methyl iodide (C.P.) was also obtained from the Eastman Kodak Company, in sealed glass bottles.

Methyl fluoride was not available from any chemical manufacturing company, and therefore it was necessary to find an efficient laboratory method for its preparation in a sufficiently pure state for spectroscopic work. The best method of preparation found was as follows: Potassium fluoride, hydrate, $KF \cdot 2H_2O$, (Baker), was heated until the water of crystallization had boiled off, leaving a white mass of anhydrous potassium fluoride, KF. This was pulverized. Potassium methyl sulfate, crystalline, KCH_3SO_4 (Eastman), was pulverized, and mixed with the pulverized potassium fluoride in the ratio—two parts KF to five parts KCH_3SO_4. The mixture was heated to 140–200°C. The gas evolved was passed: (1) through concentrated sulfuric acid in a spiral wash bottle with a gas path of about 65 cm, (2) through a concentrated solution of potassium hydroxide, (3) through a drying tube of soda lime and two drying tubes of calcium chloride (fused), and, (4) into a condenser submerged in liquid air.

The impurities which might be expected from reactions occurring in heating $KF + KCH_3SO_4$ are CO_2, H_2O, $(CH_3)_2O$, C_2H_4 and SO_2. The KOH takes out the CO_2 and SO_2 quantitatively while the $CaCl_2$ removes the H_2O. A spectroscopic test by the method of infra-red absorption was made for the possible impurities $(CH_3)_2O$ and C_2H_4. In this, the spectral region extending from 10.5μ to 11.5μ was examined. Here both $(CH_3)_2O$ and C_2H_4 absorb strongly, but methyl fluoride is transparent. When the supposed impurities were introduced into the cell at *low* pressures there was marked absorption. But when the cell was filled with methyl fluoride as above prepared, to *atmospheric* pressure, there was no measureable absorption. Hence it may be concluded that the methyl fluoride is practically free from the impurities which were feared.

Precautions were taken to secure pure materials, and furthermore, the spectra which have been obtained constitute evidence, through their regularity, that the absorption curves are not appreciably affected by impurities which might supposedly have been present.[8] This evidence becomes especially convincing when the spectra of the four compounds are considered in relation to each other.

Method of Observation

The grating is set at equal intervals throughout the spectral region under examination. At each setting of the grating deflections are taken both with

[8] One of the bands of methyl iodide presents a possible exception to this statement. It is the band of Series *E*, Fig. 8.

the cell in the beam and out of it, the cell being mounted so that it can be raised or lowered by a control lever. Because of reflection and slight absorption by the rock-salt windows of the cell a certain apparent absorption exists with the cell empty. For each band a run was made both with the cell containing gas at a known pressure, and also with the cell rinsed with air and then evacuated to less than 1 mm pressure. The percent transmission of the cell filled with gas, divided by the percent transmission of the evacuated cell gives the true percent of absorption of the gas. From the data thus obtained, curves are plotted with grating settings as absissas and percentages of absorption as ordinates.

Preliminary explorations were made of the spectra of methyl fluoride and methyl chloride with a small prism spectrometer, and the results were plotted together with the observations made by W. W. Coblentz[9] on methyl iodide. The bands for these three substances were found to fall into regular series and it was assumed that the position of the bands of methyl bromide could be located by interpolation. Later observations with the grating spectrometer proved this assumption to be correct.

Further preliminary observations were made of all bands with the grating spectrometer, using large slit widths, and with large intervals between successive settings of the grating. This was done both to find the locations of the bands more accurately than was possible with the prism spectrometer, and also to find the amount of gas which it was necessary to have in the beam to give the best definition of the lines. Definition is best when the maximum of absorption of a band is at about fifty percent.

It is necessary to determine by trial the width of slit which is most favorable for each band. These trials were often very time consuming. As the slit width is cut down, the galvanometer deflection decreases as the square of the slit width, and the zero unsteadiness becomes a large, and intolerable percent of the total deflection. On the other hand, with too great a slit width, the fine structure of the bands becomes partially or totally obliterated. The errors of observation can be somewhat reduced by taking several deflections, but taking more than three or four is of doubtful value.

The final observations on most of the bands had to be taken between midnight and morning, since the galvanometer was too unsteady at other times. It was found necessary moreover to have the spectrometer in readiness for about an hour before beginning observations in order to allow conditions to become steady.

The spectrometer constants had been carefully determined for each of the three gratings used in another investigation which ran concurrently with this one,[10] and these constants were used in computing frequencies.

General Results

Seven distinct series of bands were found for this series of compounds. Figure 4 shows the locations of the bands, and the seven series are indicated

[9] W. W. Coblentz, Publications of the Carnegie Institution of Washington, **35**, (1905).
[10] A. Levin and C. F. Meyer, J.O.S.A. and R.S.I. **16**, 137 (1928).

by the letters A to G inclusive. The full vertical lines, series A, C, E, and F, represent $\parallel$ bands, and the dotted vertical lines, series B, D, and G, represent $\perp$ bands. The lengths of the lines are roughly proportional to the intensities of the bands, and the broken lines connect the bands of each series. The two bands of methane observed by Cooley[11] are shown at the top of the figure.

Only the first two members of series A could be observed. The two remaining members presumably lie at wave-lengths too great to be reached on account of the increasing opacity of rock-salt and the absorption due to the carbon dioxide of the atmosphere. Series B, 8.5μ to 11.3μ was completely observed. The two series A and B appear to converge toward the 7.7μ band of methane.

Two more series of bands, C and D, lie between 6.6μ and 8.0μ. When series C, which is of the $\parallel$ type is extrapolated to include a band for methane, this band will lie between 2μ and 6μ. The location of the analogous band of methane cannot be more definitely stated until the nature of the vibration

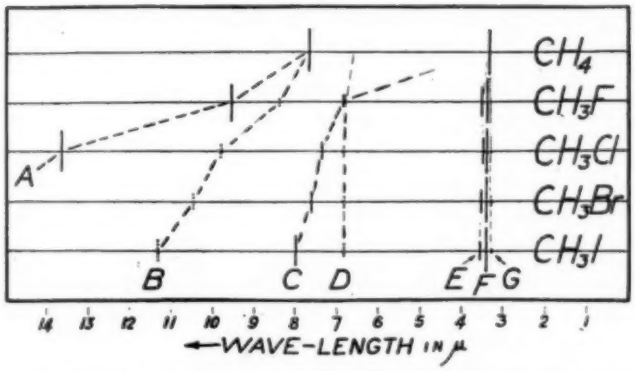

Fig. 4. Location of the bands of methane and the methyl halides.

causing this series of bands has been determined. The intensities of the bands of this series decrease toward methane and it is likely that the band of methane in this series is weak or entirely inactive.

Extrapolation of the wave-lengths of the bands of series D, which are of the $\perp$ type, toward a wave-length for methane indicates a band at about 6.6μ. The intensities decrease in this series, also toward methane. Dennison[12] predicted that an optically inactive band for methane should lie at 6.58μ. In series C, as in series B, the frequency intervals between the bands for the three heavier halides are nearly equal while that from the chloride to the fluoride is somewhat greater.

The region between 3.2μ and 3.6μ contains three series of bands, E, F, G, which converge toward the 3.31μ band of methane observed by Cooley. The central series, F, is of the $\parallel$ type and is the strongest of the three, remaining about equally strong and at nearly the same frequency throughout the series. On each side of this series is another series of bands, series E being of the $\parallel$

[11] J. P. Cooley, Astrophys, Journ. **62**, 73 (1925).
[12] D. M. Dennison, Astrophys. Journ. **62**, 84 (1925).

type and series G of the $\perp$ type. The intensities in these two series increase toward methane.

Individual Series

Series A, $\parallel$ type. The 9.55μ band for CH_3F is shown in Fig. 5 and the frequencies of the lines, as observed, are given in Table I. In the figure, the full line passes through all the points found experimentally while the dotted lines show slight idealizations which are thought to be well justified. This

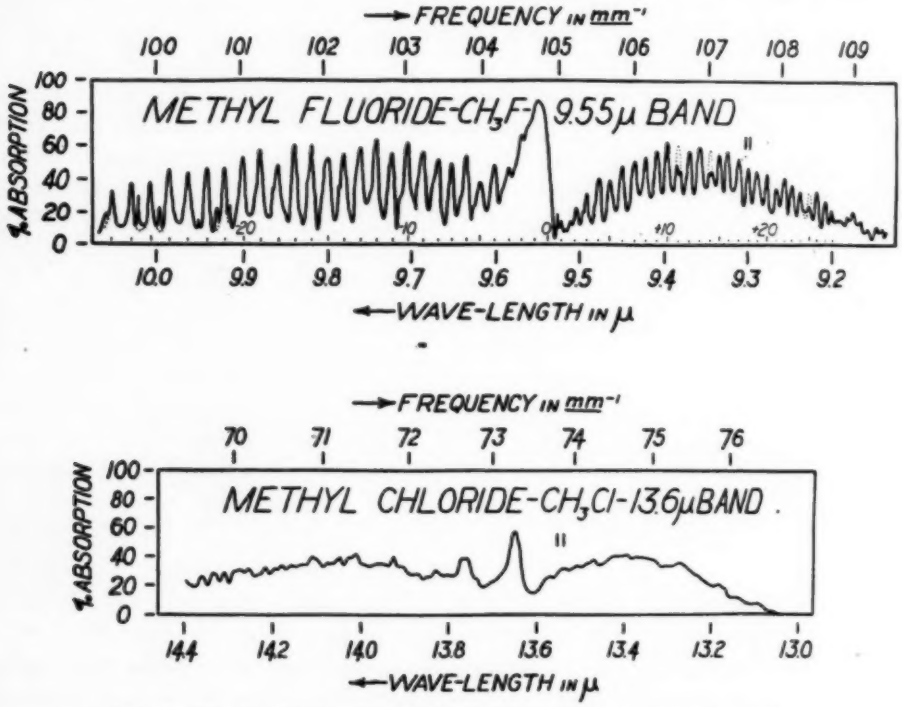
FREQUENCY IN mm⁻¹
100 101 102 103 104 105 106 107 108 109
% ABSORPTION
METHYL FLUORIDE-CH₃F-9.55μ BAND
10.0 9.9 9.8 9.7 9.6 9.5 9.4 9.3 9.2
WAVE-LENGTH IN μ
FREQUENCY IN mm⁻¹
70 71 72 73 74 75 76
METHYL CHLORIDE-CH₃Cl-13.6μ BAND
14.4 14.2 14.0 13.8 13.6 13.4 13.2 13.0
WAVE-LENGTH IN μ

Fig. 5. The bands of series A which are accessible to measurement.

Table I. *The band of methyl flouride, Series A, $\parallel$ type.*

Line No.	Observed Frequencies	Line No.	Observed Frequencies	Line No.	Observed Frequencies	Line No.	Observed Frequencies
−27	994.79cm^{-1}	−13	1024.63cm^{-1}	+ 1	—	+15	1071.21cm^{-1}
−26	997.04	−12	1026.58	+ 2	1052.24cm^{-1}	+16	1072.40
−25	999.28	−11	1028.56	+ 3	1053.57	+17	1073.97
−24	1001.50	−10	1030.60	+ 4	1055.15	+18	1075.21
−23	1003.73	− 9	1032.41	+ 5	1056.60	+19	1076.42
−22	1005.95	− 8	1034.40	+ 6	1058.21	+20	1077.90
−21	1008.03	− 7	1036.13	+ 7	1059.88	+21	1079.10
−20	1010.21	− 6	1038.00	+ 8	1061.31	+22	1080.24
−19	1012.24	− 5	1039.83	+ 9	1062.79	+23	1081.25
−18	1014.50	− 4	1041.58	+10	1064.18	+24	1082.50
−17	1016.55	− 3	1043.50	+11	1065.70	+25	1083.70
−16	1018.59	− 2	1045.02	+12	1067.19	+26	1084.81
−15	1020.62	− 1	—	+13	1068.59	+27	1086.04
−14	1022.60	0	(1048.52)	+14	1069.96	+28	1086.91

band was measured with the fluoride at a pressure of 4.0 cm. A scale is included in the figure for numbering the lines, the scale being so chosen that the number of a line is also the value of the quantum number m of the initial state in the transition which gives rise to the line. The slit width used covered a spectral range of 40A, and readings were taken at intervals of 25A.

The observed frequencies of the lines can be expressed as a quadratic function of the line number. With the frequency expressed in waves per centimeter the equation found is:

$$\nu = 1048.52 + 1.688m - 0.01125m^2$$

The differences between the observed and calculated values do not show systematic trend. If it were possible to observe the frequencies much more accurately it would probably be necessary to introduce a cubic term, but this could hardly be greater than 1×10^{-5}.

From the simple theory it was predicted that the lines should be linearly spaced, and the presence of a term of higher order implies a perturbation between the vibrational and rotational motion. Perturbation also gives varying values for the frequencies of the lines in the Q branch corresponding to the various values of the rotational quantum number, giving a Q branch which extends away from the fundamental frequency quite considerably. It is seen in the band for CH_3F that the Q branch rises steeply to a maximum value and then slopes off less steeply toward the P branch. This indicates a relatively large frequency interval between the successive unresolved lines of the Q branch.

The 13.6μ band of CH_3Cl is also shown in Fig. 5. The power of the spectrometer, although decidedly greater than that of spectrometers used heretofore, was not sufficient to define the lines of this band. Using the same slit width and taking readings at the same interval as for the 9.55μ band of CH_3F, it was found that the deflections were too small to be dependable, the available energy being smaller in this region. Using a slit-width of 60A and taking a large number of readings at each setting of the circle, it was found that a suggestion of the fine structure could be obtained but the definition was not sufficient to make a complete measurement of the band in this manner worth while. The envelope shown in the figure was measured with the gas in the cell at a pressure of 4.0 cm and using a slit width of 160A. It is to be noted in this band, as in the previous one, that the P branch extends over a greater range of frequency than the R branch, indicating that there is a large perturbation between vibrational and rotational motion also in the case of this compound.

The bands of series A for CH_3Br and CH_3I are not accessible to measurement, as has already been mentioned.

The frequencies for the maxima of the envelopes of the branches for the two bands of this series which were measured are given at the head of Table IV.

Series B, $\perp$ type. The bands range from 8.5μ to 11.3μ. They are shown in Fig. 6 and the frequencies of the Q branches as observed are given in Table II.

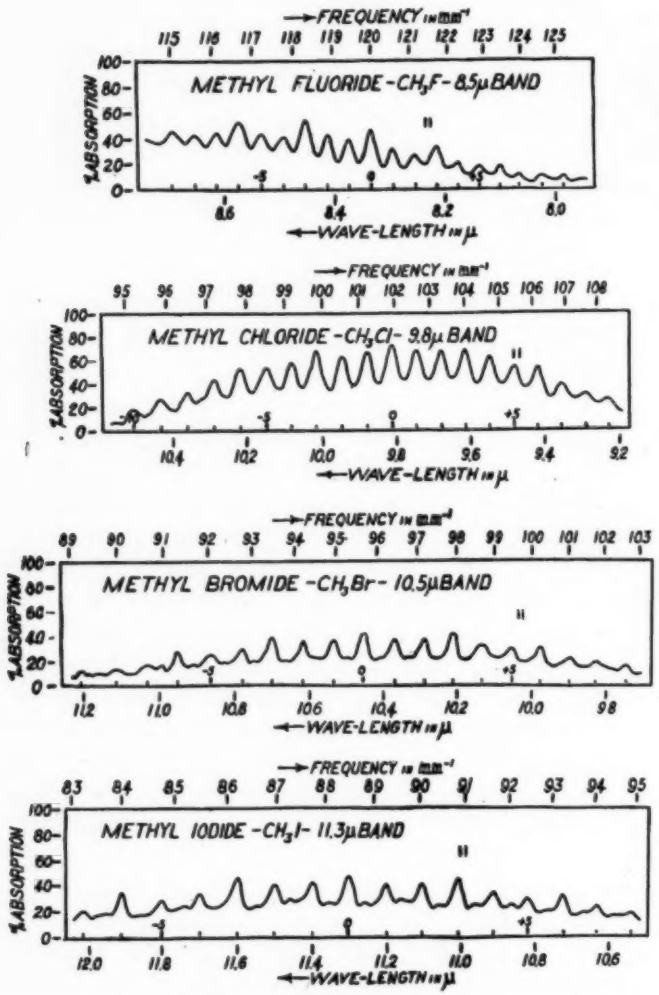
FREQUENCY in mm⁻¹
METHYL FLUORIDE - CH₃F - 8.5μ BAND
% ABSORPTION
WAVE-LENGTH in μ
METHYL CHLORIDE - CH₃Cl - 9.8μ BAND
METHYL BROMIDE - CH₃Br - 10.5μ BAND
METHYL IODIDE - CH₃I - 11.3μ BAND

Fig. 6. The bands of series B.

TABLE II. *The bands of series B, ⊥ type.*

Line No.	Observed frequencies, cm^{-1}. CH_3F	CH_3Cl	CH_3Br	CH_3I	Line No.	Observed frequencies, cm^{-1}. CH_3F	CH_3Cl	CH_3Br	CH_3I
−10		952.6			0	1200.0	1019.9	956.9	885.1
− 9	1150.6	958.8	892.3		1	1206.0	1026.7	964.6	892.8
− 8	1155.6	965.7	899.8		2	1211.6	1033.6	972.0	900.7
− 7	1160.9	972.4	906.5	832.5	3	1217.0	1040.6	979.3	908.6
− 6	1166.4	978.9	913.3	840.0	4	1222.8	1047.9	986.8	916.4
− 5	1172.2	985.6	920.7	847.6	5	1228.4	1055.3	994.9	924.4
− 4	1177.6	992.3	927.8	854.9	6	1234.2	1062.1	1002.5	932.6
− 3	1183.1	999.0	934.8	862.4	7	1240.0	1069.5	1010.5	940.6
− 2	1188.7	1006.0	942.3	869.7	8	1246.1	1076.7	1018.1	949.0
− 1	1194.3	1012.9	949.5	877.5	9	1252.5	1083.8	1026.5	

In the curve for CH_3F it will be noted that the background of absorption rises continuously in the direction of greater wave-length. This band was observed with the gas in the cell at a pressure of 72.1 cm; it is thus much fainter than the neighboring band of series *A* at 9.55μ which was observed at a pressure of 4.0 cm. By raising the pressure from 4.0 cm to 72.1 cm the effective width of the band at 9.55μ of course increases very materially. By extending the measurements with the gas at a pressure of 72.1 cm beyond the limits of the curve represented for the 8.5μ band it was definitely established that the rising background was due to overlapping with the 9.55μ band which was broadened and intensified by the increased gas pressure. If it were not for this overlapping the maximum of absorption attained in the 8.5μ band would probably have been about 45 percent instead of about 55 percent as represented.

The band for CH_3Cl was measured at a pressure of 74.0 cm. It shows a percent absorption much greater than that of the band for CH_3F and hence the conclusion may be drawn that it is more intense than the latter, although less intense than the band for CH_3Br which was measured at 22.3 cm pressure. The band for CH_3I was measured at 21.8 cm pressure and appears to be the most intense band of the series. Slit-widths used in this region ranged between 100A and 200A.

In all of these bands, every third line is more intense than the others. Between the lines in the band for CH_3I and less pronouncedly in the band for CH_3Br, there appear faint lines. Repeated measurements of these intervals between the principal lines showed these faint lines to be real.

The positions of the principal lines converge, in the direction of *lower* frequencies. Expressed in waves per cm the positions can be represented by the following equations:

$$\text{for } CH_3F \quad \nu = 1200.10 + 5.650\, n + .015\, n^2$$
$$\text{“ } CH_3Cl \quad \nu = 1019.70 + 6.945\, n + .022\, n^2$$
$$\text{“ } CH_3Br \quad \nu = 957.00 + 7.420\, n + .030\, n^2$$
$$\text{“ } CH_3I \quad \nu = 885.15 + 7.700\, n + .032\, n^2$$

Since the coefficients of the quadratic terms are large, the perturbations are large for this type of vibration, also. It will be noted further that the coefficients of the quadratic terms become larger with increased atomic weight of the atom substituted in methane, which indicates that perturbations are somewhat larger in the cases of heavier atoms.

Series C, $\parallel$ type, and D, $\perp$ type. The two series of bands, which lie in the region of 7μ, are shown in Fig. 7. The bands of series *C* have unresolved *P*, *Q*, and *R* branches. In the three lower curves they lie on the left of the figure, and may be readily identified. In the upper curve, for CH_3F, the bands of series *C* and *D* are superposed. The bands of series *D* on the right, consist of a succession of *Q* branches. The frequencies of these are given in Table III. There are falsifications introduced into the measurements for this series of bands due to the fact that the water vapor of the atmosphere absorbs strongly in the region in which the bands lie. These falsifications are produced in three ways.

First, the available energy at certain settings of the grating is extremely small, causing the errors of observation to rise correspondingly. Second, the slit passes a range of wave-length which is somewhat greater than the width

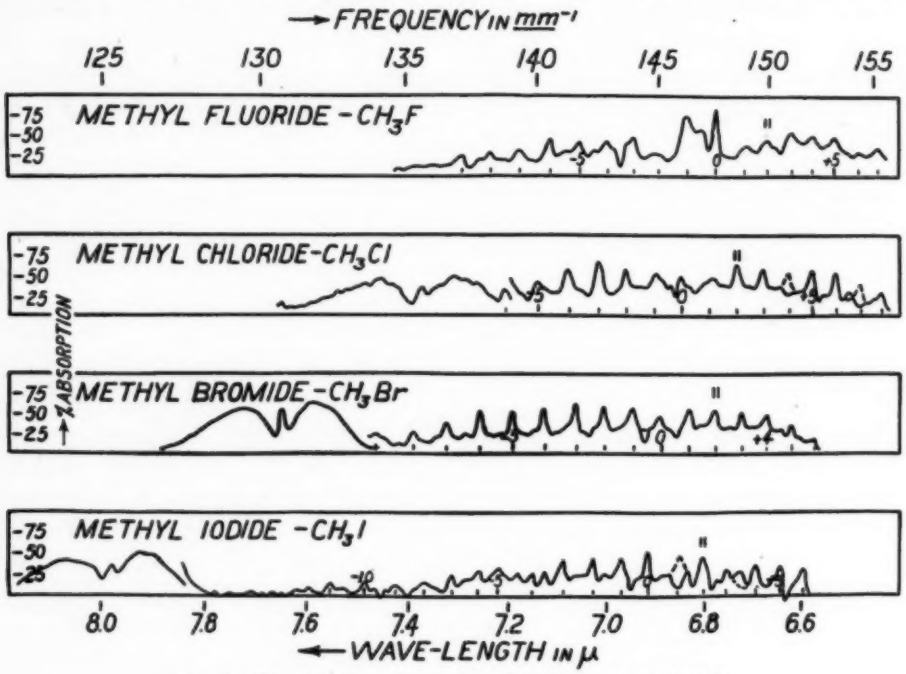

Fig. 7. The bands of series C (left) and series D (right).

of a line in either the water vapor or the methyl halide spectrum. If a line in each of these spectra happens to come at just the same wave-length, no great decrease in energy transmitted by the slit is noted although the line in the

TABLE III. *The bands of series D, ⊥ type.*

Line No.	Observed frequencies, cm^{-1}. CH_3F	CH_3Cl	CH_3Br	CH_3I	Line No.	Observed frequencies, cm^{-1}. CH_3F	CH_3Cl	CH_3Br	CH_3I
−11				1323.7	−1	1463.8	1447.5	1438.7	1434.8
−10				1335.6	0	1475.7	1459.6	1450.5	1445.5
− 9	1371.6		1339.0	1346.7	1	1487.9	1471.9	1463.0	—
− 8	1381.7		1352.4	1356.9	2	1499.0	1484.3	1474.7	1470.1
− 7	1392.7		1364.7	1367.6	3	1510.5	1496.7	1486.7	1480.5
− 6	1404.8	1387.0	1377.5	1378.2	4	1521.1	—	1498.2	1494.0
− 5	1416.9	1399.5	1390.0	1385.5	5	1531.6	1519.8	1509.5	1505.6
− 4	1428.2	1412.4	1402.3	1398.3	6	1542.0	1531.6	1520.3	1515.9
− 3	1439.5	1424.3	1415.3	1410.6	7	1551.0	—		
− 2	1451.5	1435.9	1426.7	1422.9	8		1554.0		

methyl halide spectrum at this wave-length may be quite intense. Third, there is an effect due to the very steep slopes in the energy curve which are present in a region of water vapor absorption, considered in conjunction with

minute alterations of the beam which occur when the absorption cell is introduced. The explanation of this effect is involved, and will not be given in detail.

Slit widths corresponding to about 70A were used, and readings were taken at an interval of about 75A. Measurements were also made on the $\parallel$ band for the chloride using a slit width of 35A and taking a large number of readings at each point. These measurements showed a suggestion of fine structure, but not a sufficient one to justify continuing the measurements with this slit width. The pressures of gas in the cell are given in Table V. For the band of Series *D* of methyl iodide it was necessary to use a special cell for reasons which will be given presently.

The positions of the *Q*-branches in series *D* are not as accurately given as those of series *B*. The observed data for CH_3F and CH_3I fall too irregularly to allow conclusions to be drawn in regard to convergence. The data for CH_3Cl and CH_3Br however indicate a convergence of the lines in the direction of *higher* frequencies. But the irregularities are too great to permit giving expressions for the frequencies in which the quadratic terms would have significance. The linear terms (average intervals between the lines) are given in Table VIII.

TABLE IV. *Maxima of the envelopes of the branches,* $\parallel$ *bands.*

	Observed frequencies			Doublet Spacing $\nu_P - \nu_R$
	P-branch	*Q*-branch	*R*-branch	
Series *A*				
CH_3F	1023cm^{-1}	1048.5cm^{-1}	1066cm^{-1}	43cm^{-1}
CH_3Cl	712	732.3	747	35
Series *C*				
CH_3F	—	1475.7	—	—
CH_3Cl	1341	1355.3	1369	28
CH_3Br	1293	1305.5	1318	25
CH_3I	1240	1251.8	1263	23
Series *E*				
CH_3F	2841	2862.4	2985	44
CH_3Cl	2868	2879.6	2891	23
CH_3Br	2850	—	2873	23
CH_3I	2851	—	2872	21
Series *F*				
CH_3F	—	2965.3	—	—
CH_3Cl	2953	2967.0	2981	28
CH_3Br	2961	—	2984	23
CH_3I	2960	(2970.6)	2981	21

Series E and F, $\parallel$ *type, and G,*$\perp$ *type.* The three series of bands, lying in the 3μ region are shown in Fig. 8. The bands of series *E* and *F* have unresolved *P*, *Q*, and *R* branches. The *Q* branches are strong only in the case of the fluoride. For the other three compounds they are weak, and in some cases are not recorded. The frequencies of the maxima of the envelopes of the branches are given in Table IV. The frequencies of the succession of *Q*

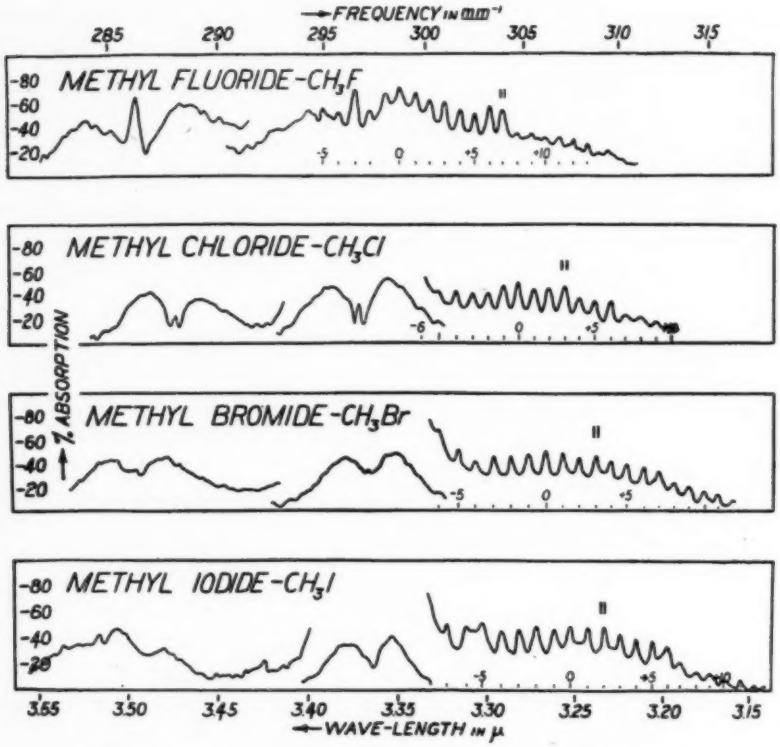

Fig. 8. The bands of series E (left), F (center), and G (right).

TABLE V. *Pressures of gas in absorption cell.*

	Series *C*	Series *D*
CH_3F	31.4 cm	31.4 cm
CH_3Cl	11.3	30.8
CH_3Br	8.3	28.3
CH_3I	11.9	40. (10 cm cell)

TABLE VI. *The bands of series G, ⊥ type.*

Line No.	Observed frequencies, cm^{-1}. CH_3F	CH_3Cl	CH_3Br	CH_3I	Line No.	Observed frequencies, cm^{-1}. CH_3F	CH_3Cl	CH_3Br	CH_3I
−7		2989.0		3009.4	3	3009.6	3071.7	3088.2	3100.9
−6	2942.6	2998.2	3005.5	3019.3	4	3017.7	3079.6	3096.6	3109.9
−5	2949.4	3006.5	3015.3	3027.5	5	3024.9	3087.8	3104.5	3118.8
−4	2957.2	3015.4	3023.8	3037.5	6	3032.5	3096.7	3113.9	3127.3
−3	2965.3	3024.2	3034.3	3046.8	7	3039.2	3104.6	3122.3	3134.5
−2	2972.3	3031.7	3042.8	3056.2	8	3047.3	3112.5	3131.0	3143.8
−1	2980.2	3039.8	3052.3	3065.4	9	3054.5	3121.0	3138.6	3151.4
0	2987.2	3047.2	3061.5	3074.2	10	3061.3	3129.2	3147.2	3159.2
1	2995.0	3055.5	3070.2	3083.6	11	3068.8		3155.2	3168.9
2	3002.2	3063.2	3079.3	3092.4	12	3076.5		3163.8	3176.8
					13	3083.8			

branches in the bands of series G are given in Table VI. In the case of the fluoride the bands of series F and G overlap, as do the aforementioned bands of series C and D for this compound. The greater intensity of every third line is again noticeable in series G, but it is less evident than in series B, Fig. 6. The failure to record the intensification of every third line in series D, Fig. 7, may well be due to the falsification introduced by the water vapor of the atmosphere.

Slit widths of from 30A to 43A were used and readings were taken at an interval of 17A. The pressures of gas in the cell are given in Table VII. The bands for the iodide in series D, E, and G are weak and it was necessary to use

TABLE VII. *Pressures of gas in absorption cell.*

	Series E	Series F	Series G
CH_3F	14.4 cm	6.4 cm	6.4 cm
CH_3Cl	19.5	5.0	17.4
CH_3Br	23.9	5.3	50.5
CH_3I	40. (10 cm cell)	10.0	40. (20.8 cm cell)

a cell of greater length than the one of 6 cm which has otherwise been used throughout. A cell of variable length with mica windows and carefully selected compensating windows was available. All of the windows made an angle of 30° with the beam to avoid interference effects which occur when the thin windows are used perpendicularly to the beam.[13] For the band in series E the cell was adjusted to a length of 10 cm, and it was allowed to fill with the saturated vapor of the iodide by letting it stand for a day with a small flask of liquid iodide in the cell at 25°C. The vapor pressure of methyl iodide at this temperature is 40 cm. For the band in series G, the cell was adjusted to a length of 20.8 cm and the same procedure was followed. The band of series E for the iodide does not present a clear structure. Because of a fear that mica interference effects might still be present, measurement of this band was repeated using a cell with rock salt windows, having a length of 10 cm. Practically the same curve was obtained.

The Q branches, in series G, converge in position in the direction of *higher* frequencies. Moreover, the convergence increases in passing from the fluoride to the chloride, the bromide, and the iodide, indicating again larger perturbations in the cases of heavier atoms. The observed data when plotted do not, however, have sufficient regularity to justify giving expressions for the frequencies involving quadratic terms. The average intervals between the lines are given in Table VIII.

In the bands of series E and F the intensities of the Q branches diminish in passing through each series from the fluoride to the iodide, or from the lighter to the heavier halide, a circumstance which may be understood by applying the intensity expression found by Dennison, Reiche and Kronig.[1]

[13] C. F. Meyer and D. W. Bronk, Astrophys. Journ. 59, 252 (1924).

The bands of series E for the chloride, bromide, and iodide progress quite regularly toward the wave-length, 3.31μ, found by Cooley[11] for the band of methane in this region, while the band of the fluoride is somewhat out of position. It was thought that perhaps this band was a member of still another series, fainter than these three, whose bands lay at longer wave-lengths for the compounds with higher atomic weight of the substituted atom. Explorations to 4.5μ with the cell filled to atmospheric pressure with CH_3Cl showed no absorption, so it was concluded that this band of CH_3F must be a quite irregularly placed member of series E.

Comparison Between Series

The frequency intervals between the points of maximum absorption of the P and R branches in the bands of the $\parallel$ type are on the whole the same for the bands of any compound in different series. This frequency interval is commonly referred to as the doublet separation of the band. For the fluoride, it has been possible to determine the doublet separation for only two bands because of the overlapping of the remaining two bands of the $\parallel$ type with those of the $\perp$ type. The two doublet separations which have been determined agree to within the experimental accuracy. The four doublet separations recorded for the chloride do not agree, but range in value from 35 cm^{-1} for the band of series A, to 23 cm^{-1} for the band of series E, exhibiting a divergence which may or may not be real. Those for the bromide and iodide agree as nearly as they can be determined. Table IV gives the doublet separations for all the bands which could be measured.

The simple theory predicts that the frequency interval between the Q branches in the bands of the $\perp$ type for each compound will be the same for all the bands of this type for the compound. It has been found, however, that this is not the case. Table VIII gives the average interval between the lines

Table VIII. *Average frequency intervals between lines.*

Methane, CH_4	5.4 cm^{-1} (region of 7.7μ)		9.8 cm^{-1} (region of 3.3μ)
Methyl halides	Series B	Series D	Series G
CH_3F	5.65 cm^{-1}	11.5 cm^{-1}	7.5 cm^{-1}
CH_3Cl	6.95	12.0	8.2
CH_3Br	7.42	11.9	9.0
CH_3I	7.70	11.8	9.0

in the bands of all the regions observed. The separations of the lines for the bands in series D are seen to be nearly twice those of the bands of series B for corresponding compounds, while the separations in series G have intermediate values.

It appears that the explanation of this phenomenon must come from a deeper understanding of the mechanism of this type of vibration and its interactions with rotation. It is clear, however, from the general form of the spectrum that the methyl halide molecule must be of the symmetrical type,

and in fact, recourse to an unsymmetrical model having three different moments of inertia would in no way serve to explain either the general features of the spectrum or the structure of the $\perp$ bands.

In conclusion the authors wish to acknowledge their indebtedness to Professor D. M. Dennison, who has given liberally of his time and energy in studying and discussing the interpretation of the experimental results.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF MICHIGAN,
AUGUST, 1928.

Note added to proof, Oct. 27th: Professor Firestone has recently taken some Raman spectrograms of methyl bromide and methyl iodide, in liquid form, from which it was hoped to determine the positions of the bands of Series *A* for the two compounds. These bands have eluded detection by direct infra-red methods, as above mentioned. The first photographs, while showing Raman lines, do not permit definite conclusions to be drawn. It is hoped that an announcement of the results may shortly be made in the form of a note in this journal.

VISIBLE ABSORPTION BANDS OF COLORLESS LIQUIDS AND THEIR RELATION TO INFRA-RED BANDS

By Joseph W. Ellis

Abstract

The absorption of ten representative organic liquids has been studied in the visible spectrum by photographic means. Cell lengths up to 6½ meters were employed. The near infra-red spectra of these same substances have been obtained. A good correlation of the bands of the two regions has been secured; the bands of the visible region seem to be higher members of series previously detected in the infra-red.

THERE seems to have been no recent extensive study of the absorption bands of colorless liquids in the visible region of the spectrum. Nearly fifty years ago Russell and Lapraik[1] published the results of an investigation of the absorption of twenty-nine substances, mainly organic liquids, in the region between 0.73μ and 0.5μ. By using cell thicknesses varying from 2 to 8 ft. they were able to observe one or more absorption band for each substance. Their observations were made visually with a prism spectroscope and their results were presented through drawings.

The writer's apparent ability to formulate certain bands in the infra-red absorption spectra of various organic compounds into series which approach the red of the visible spectrum has caused him to attempt to correlate the bands of the visible region with those of the near infra-red. It seemed advisable to check some of the observations of Russell and Lapraik and also to extend the study to other compounds not examined by those investigators.

A large Hilger quartz spectrograph of the E1 type was used in the photography of these spectra. The source for a continuous spectrum was a 400 watt lamp. The absorption cells, ranging in length from 78 cm to 650 cm, were made by joining together sections of Pyrex glass tubing of about 20 mm inside diameter. These sections were silvered inside to increase the amount of light transmitted through the tube and to remove the possibility of introducing extraneous bands due to absorption by the glass walls. The ends of each tube were faced with bakelite cemented to the glass with deKhotinsky cement. The sections were held together with inside threaded brass sleeves and outside threaded brass collars cemented to the opposite tube. The two end sections were equipped with removable quartz end-plates. The light was rendered parallel before traversing the cell, but no condensing lens was used between the cell and the spectrograph slit.

Three types of photographic plate were used: orthochromatic, panchromatic and extreme red sensitive. No one type of plate is sensitive to the whole region under investigation. The use of extreme red sensitive plates permitted photography in the region of 0.75μ, a region not attained by Russell and Lapraik.

[1] Russell and Lapraik, Nature **22**, 368 (1880); Jour. Chem. Soc. **39**, 168 (1881).

The substances used for this study were chosen to include certain definite types of molecules. One purpose of the investigation was to observe the effects of unsaturation and of substitution in the molecule. Since great cell lengths were employed the number and types of compounds studied were limited by the cost of materials. Those used are discussed individually in the following paragraphs.

The plates were measured with a specially constructed measuring box equipped with a scale with a vernier attachment reading to 1/20 mm. Hartmann's dispersion formula was used to measure the lines by interpolation between helium and Fraunhofer lines. The sensitiveness of the instrument was equivalent to about 0.0002 and 0.0004μ in the regions 0.6μ and 0.75μ respectively, but because of the finite widths of the bands an accuracy of only about 0.001μ can be claimed.

Hexane, C_6H_{14} (E. K. Co. #P1135); 78 and 355 cm cell. This was chosen as the most readily obtained saturated chain hydrocarbon. A single band at 0.558μ (probably one component of a doublet) and two double bands at 0.635, 0.649μ and 0.744, 0.760μ were recorded. The shorter wave-length members of the double bands were the more intense.

Cyclohexane, C_6H_{12} (E. K. Co. #P702); 78 and 445 cm cell. This is a saturated cyclic hydrocarbon. It showed three double bands of approximately equal intensity components: 0.567, 0.575μ; 0.644, 0.653μ; and 0.753, 0.763μ. Bands characteristic of benzene appeared and were assumed to be due to this substance as an impurity.

Benzene, C_6H_6 (thiophene free); 78, 355 and 650 cm cell. This unsaturated cyclic hydrocarbon gave the following bands, all of which were single: 0.476, 0.532, 0.608 and 0.712μ. The 0.476μ band was extraordinarily weak even with the 6.5 m cell, but was detected on two different plates by several observers. It is of a shorter wave-length than any band observed by Russell and Lapraik.

Toluene, $C_6H_5 \cdot CH_3$ (E. K. Co. #P325); 78, 170 and 631 cm cell. The effect of substitution of a methyl group was sought in this instance. Bands of the benzene type were observed at 0.608μ and 0.713μ. In addition a weak double band at 0.737, 0.748μ was found. The rather nebulous absorption recorded by Russell and Lapraik around 0.63μ could not be brought out.

m-Xylene, $C_6H_4 \cdot (CH_3)_2$ (E. K. Co. #T275); 78, 170 and 436 cm cell. The bands characteristic of the benzene ring were found shifted to 0.611μ and 0.713μ. A doublet at 0.738, 0.748μ was much more intense than the one analogous to it in toluene. Absorption occurs near 0.63μ but, because of the low sensitivity of the plates, no measurements could be made upon it. There seems, however, to be evidence of doubleness there.

Chlorobenzene, C_6H_5Cl (E. K. Co. #70); 70 and 353 cm cell. The benzene bands appeared, shifted to shorter wave-length values, 0.604μ and 0.707μ.

Chloroform, $CHCl_3$ (Eastman practical and U.S.P.); 78, 170 and 445 cm cell. The following bands were found: 0.614, 0.622, 0.665, 0.690 and 0.721μ.

Acetone, $CH_3 \cdot CO \cdot CH_3$ (E. K. Co. #P297); 78, 170 and 449 cm cell. Two doublets with the shorter wave component slightly more intense were observed: 0.618, 0.631μ and 0.727, 0.741μ.

Ethyl acetate, $CH_3COOC_2H_5$ (E. K. Co. #300); 78 and 263 cm cell. This compound showed two doublets, the shorter wave members being the weaker: 0.617, 0.626μ and 0.723, 0.735μ.

Aniline, $C_6H_5 \cdot NH_2$; 78, 172 and 353 cm cell. This sample was obtained from the chemistry department. It was twice distilled before using but retained a slightly yellow color. Light transmitted through it varied in color from a deep red to a bright orange for cell lengths ranging from 353 to 78 cm. This compound was included in order to observe the effects due to the substitution of an amino group. Bands were found at 0.608, 0.648 and 0.712μ. A prominent one at 0.630μ found in Russell and Lapraik's spectrum of aniline, as well as in certain of their other records, does not appear in this investigation. The absence of this band is of interest since it is one of the few among all of those observed by these investigators which finds no place in the correlation described later in this article.

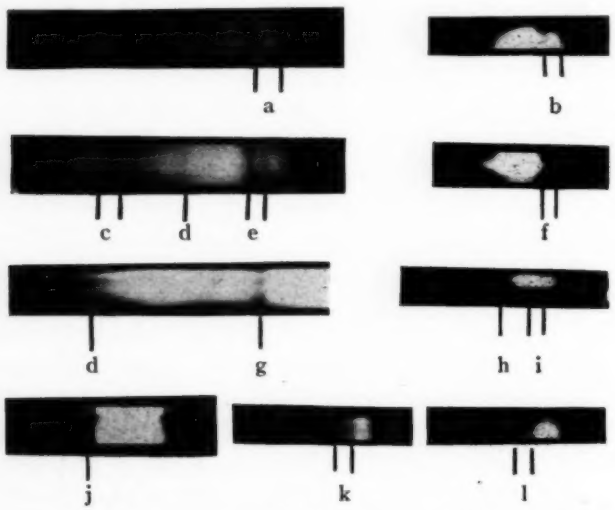

Fig. 1. Typical visible absorption bands—*a*, Hexane 0.635, 0.649μ; *b*, Hexane 0.744, 0.760μ; *c*, Cyclohexane 0.567, 0.575μ; *d*, Benzene 0.608μ; *e*, Cyclohexane 0.644, 0.653μ; *f*, Cyclohexane 0.753, 0.763μ; *g*, Benzene 0.608μ; *h*, m-Xylene 0.713μ; *i*, m-Xylene 0.738, 0.748μ; *j*, Chlorobenzene 0.707μ; *k*, Acetone 0.727, 0.741μ; *l*, Ethyl acetate 0.723, 0.735μ.

Of the above substances Russell and Lapraik give records for benzene, toluene, xylene, chlorobenzene, aniline and chloroform. There seems to be a good agreement among the results of the two investigations; however, it is evident that there is a systematic error of calibration in the red on the part of the earlier investigators. That their published values for the region 0.7μ are too low is evident by comparing their 0.708μ value for benzene and toluene with the 0.713 and 0.714μ values for these substances obtained by Barnes and Fulweiler[2] through the use of a diffraction grating. The values of the present investigation are nearly in agreement with those of Barnes and Fulweiler,

[2] Barnes and Fulweiler, Jour. Amer. Chem. Soc. 49, 2034 (1927).

but differ consistently from those of Russell and Lapraik in this particular portion of the spectrum.

Since the present investigation includes an attempt at correlation of these visible bands with infra-red bands, the spectra below 2.5μ of all of the above

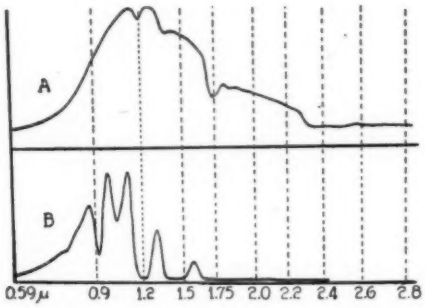

Fig. 2. Hexane. *A*, 1 mm; *B*, 155 mm.

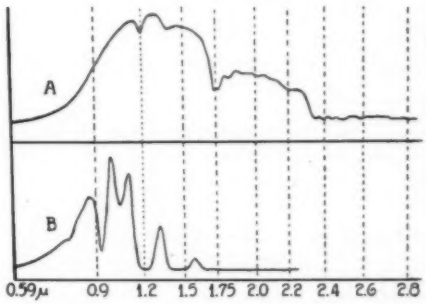

Fig. 3. Cyclohexane. *A*, 1 mm; *B*, 155 mm.

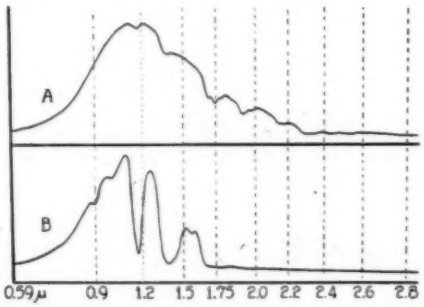

Fig. 4. Acetone. *A*, 1 mm; *B*, 155 mm.

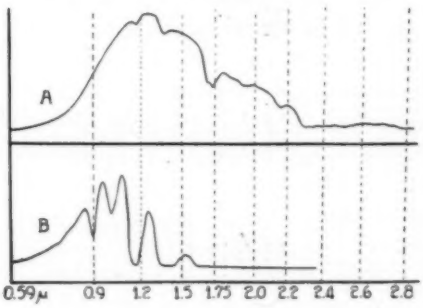

Fig. 5. Ethyl acetate. *A*, 1 mm; *B*, 155 mm.

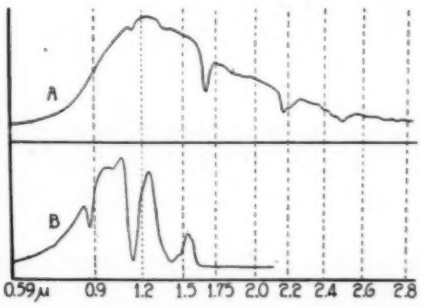

Fig. 6. Chlorobenzene. *A*, 1 mm; *B*, 155 mm.

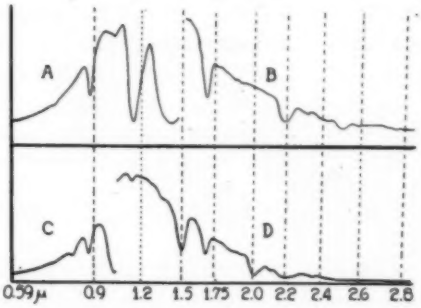

Fig. 7. *A*, Benzene, 1 mm; *B*, Benzene, 155 mm; *C*, Aniline, 1 mm; *D*, Aniline, 155 mm.

compounds were carefully recorded on a registering quartz spectrograph. Two cell thicknesses, 155 mm and 1 mm, were used to bring out the bands most advantageously. The records of all of these substances, with the exception of chloroform, are shown in Figs. 2–8. Where data for wave-lengths greater

than 2.5μ were needed, the values were taken from the published papers of other investigators, references to which are given in connection with Table I.

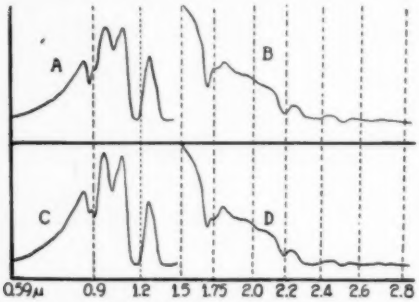

Fig. 8. *A*, Toluene, 1 mm; *B*, Toluene, 155 mm; *C*, m-Xylene, 1 mm; *D*, m-Xylene, 155 mm.

In 1881 Abney and Festing[3] published the results of a photographic investigation of the spectra of a group of compounds in the short wave portion of the infra-red. Although it is possible to associate certain of their bands with those usually found below 1μ by thermal means, the complexity of the spectra which they record seems not to be in general agreement with the observations of others. Because of this no use is made of their data in the present paper, even in those few instances in which a substance was studied in both investigations.

In earlier papers[4] the writer attempted to arrange certain of the near infra-red absorption frequencies of a few organic compounds into a series whose constants were evaluated from an average of the frequencies observed for several compounds. Variations in the positions of these bands which are quite certainly due to molecular structure make this method of formulation extremely inadvisable. This series included nine members ranging from about 6.5μ to 0.76μ. A later note,[5] preliminary to the present paper, attempted to reformulate for individual compounds certain of these bands into new parabolic series which include most of the bands observed in the visible spectrum. The new series, with initial members near 3.3μ and 3.4μ respectively for aryl and alkyl compounds, include only alternate bands of the older series. There are three main reasons for this reformulation. (1) Only the alternate bands chosen bear a similarity in structure to one another. (2) Only under these circumstances does a series yield a sequence of bands of gradually diminishing intensities. (3) The bands of the visible region fit into this arrangement.

In Table I are tabulated the wave-length values of the members of these series. The values of n refer to the series member number; this reaches the maximum value of 8 for the 0.476μ band found in the visible blue of the benzene spectrum. Data from observations by others have been included in this table.

The notion initially advanced in the writer's earlier papers that these bands originate in characteristic oscillation frequencies of the carbon-hydrogen bond is retained here. Infra-red bands other than those tabulated recur in the spectra of these compounds and doubtless are somehow associated with the C-H linkage. They will not be discussed in this article. The above series, however, include all of the observed visible bands with the exception of the 0.622, 0.665 and 0.690μ values of chloroform and the 0.648μ value for aniline.

[3] Abney and Festing, Phil. Trans. **172**, 887 (1881).
[4] Ellis, Phys. Rev. **23**, 48 (1924); **27**, 298 (1926); J.O.S.A. and R.S.I. **8**, 1 (1924).
[5] Ellis, Phys. Rev. **31**, 310 (1928).

TABLE I. *Wave-length values in μ of infra-red and visible absorption bands.*

	n=1	2	3	4	5	6	7	8
Hexane	3.48, 3.39 a; 3.43 b	1.76, 1.73; 1.73 c	1.195; 1.19 c	0.92	0.760, 0.744	0.649, 0.635	....., 0.558	.....
Cyclohexane	3.49 c	1.765, 1.735; 1.74 c	1.20; 1.19 c	0.93	0.763, 0.753	0.653, 0.644	0.575, 0.567	
Benzene	3.26 a; 3.25 b; 3.30 c; 3.30 d	1.68; 1.68 b; 1.70 c	1.145; 1.14 b; 1.19 c; 1.13 e; 1.18 f	0.875; 0.874 g	0.712; 0.713 g; 0.708 h	0.608; 0.611 h	0.532	0.476
Toluene	3.46, 3.41 a, 3.27; 3.34 b; 3.38 c	1.77, 1.75, 1.69; 1.71 b; 1.71 c	1.19, 1.15 i; 1.19 c	0.910, 0.875; ....., 0.877 g	0.748, 0.737, 0.713; ....., 0.714 g; 0.708 h	....., 0.608; 0.612 h	.....	.....
m-Xylene	3.38 b; 3.39 c	1.77, 1.75, 1.70; 1.71 b; 1.71 c	1.19, 1.15 i; 1.19 c	0.910, 0.885; 0.879 g	0.748, 0.738, 0.713; 0.710 h	....., 0.611; 0.613 h	.....	.....
Chlorobenzene	3.14 c	1.67; 1.60 c	1.14	0.87	0.707; 0.708 h	0.604; 0.611 h	.....	.....
Chloroform	3.32 b; 3.10 c	1.69; 1.69 b; 1.66 c; 1.72 f	1.15 i; 1.14 c; 1.19 f	0.88	0.721; 0.714 h	0.614; 0.612 h	.....	.....
Acetone	3.42 b; 3.26 c	1.74, 1.695; 1.77 c	1.18, 1.15?; 1.14 c	0.90	0.741, 0.727	0.631, 0.618	.....	....
Ethyl acetate	.....	1.73, 1.695	1.18	0.90	0.735, 0.723	0.626, 0.617	.....	.....
Aniline C-H	3.25 b; 3.20 j	1.68	1.145	0.87	0.712; 0.704 h	0.608; 0.611 h	.....	.....
Aniline N-H	2.80 j	1.50	1.03	0.79	0.648; 0.649 h	.....	.....	.....

a. Meyer, Bronk and Levin, J. O. S. A. and R. S. I. **15,** 257 (1927).
b. Coblentz, Publication of the Carnegie Institution of Washington, No. 35 (1905).
c. Márton, Zeits. f. Phys. Chem. **117,** 97 (1925).
d. Bell, Jour. Amer. Chem. Soc. **47,** 2811 (1925).
e. Puccianti, Phys. Zeits. **1,** 48 (1899).
f. Dreisch, Zeits. f. Physik **30,** 200 (1924).
g. Barnes and Fulweiler, Jour. Amer. Chem. Soc. **49,** 2034 (1927); J. O. S. A. and R. S. I. **15,** 331 (1927).
h. Russell and Lapraik, Jour. Chem. Soc. **39,** 168 (1881).
i. Ellis, Phys. Rev. **23,** 48 (1924).
j. Bell, Jour. Amer. Chem. Soc. **47,** 2192 (1925).

Since the infra-red spectrum of chloroform contains exceptionally strong bands apparently associated with the presence of the chlorine atoms we may

credit the above three visible absorption regions to the presence of the halogen. The 0.648μ band for aniline fits well into a second series of bands originating at 2.80 or 2.90μ which is apparently due to the N-H linkage.[6] This special series is included at the bottom of Table I. The new record for aniline yields a value of 1.50μ for $n=2$. Using a 155 mm cell a band, not characteristic of the phenyl radical appears at 0.79μ. This fits the N-H sequence as $n=4$.

A further evidence which supports the new series formulation is to be found in a succeeding paper which attempts to use these series in the evaluation of the heats of linkage of the C-H and N-H bonds.

The writer wishes to acknowledge the helpful assistance of Mr. Kenneth Stoddard in this investigation.

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UNIVERSITY OF CALIFORNIA AT LOS ANGELES.
AUGUST 14, 1928.

[6] Ellis, Jour. Amer. Chem. Soc. 50, 685 (1928).

INTENSITY MEASUREMENTS IN THE HELIUM SPECTRUM

By Clarence Hodges and W. C. Michels

Abstract

The absolute and relative intensities of thirteen lines of the helium spectrum, extending through the visible region, have been measured by a modification of the method developed by Ornstein and Dorgelo. The change of the method has consisted in comparing each line directly with the known emission from a tungsten filament, operated under constant conditions. The results for a discharge in a capillary tube, with pressures from 1.92 to 34.3 mm show that the absolute intensities increase rapidly to a maximum for pressures in the neighborhood of 2 to 4 mm, below which they tend toward zero. The relative intensities of the singlet system are favored by lowered pressures, and the higher members of the triplet system are likewise favored over the lower members, while the relative intensities within the singlet series show little effect of pressure.

THE interesting regularities which have been shown in the intensity relationships of multiplets[1] and the apparent importance of pressure conditions in the excitation of stellar spectra[2] seem to make a general study of the effect of pressure on line spectra desirable. The method developed by Ornstein and Dorgelo,[3] although its use had previously been limited largely to multiplet work, seemed to hold possibilities of extension over larger regions of wave-length, and to studies of this type.

The method, as originally developed, consists of photographing the spectrum through a series of known reducers, and thus obtaining the density-exposure curves for the lines. Over the regions used for multiplet studies, these curves were found to have a constant separation, as they followed very closely the Swartzschild law:

$$D=\gamma \log (It^p)+D_0$$

The shift of these curves along the exposure axis to bring them into coincidence made possible a determination of the photographic ratios of intensities. A correction for the sensitivity ratios of the plates, determined by similar photographs taken with a calibrated continuous source, gave the true relative intensities.

When we attempted to extend this method over the range covered in this study (3819–5876A), however, we found that γ varied between wide limits with change of wave-length, and we have modified the method by comparing each line directly with the continuous spectrum at the same wave-length, taken with identical exposure time, and on a film from the same box as those used for the line spectrum.

[1] Ornstein, Proc. Phys. Soc. London **37**, 334–347 (1925).
[2] Bowen, Astrophys. J. **47**, 1–15 (1928).
[3] Dorgelo, Phys. Zeits. **26**, 1–39 (1925).

Apparatus and Method

The source used for the helium spectrum consisted of a capillary discharge tube, having an inside diameter of 4 mm and a length of 10 cm, with hollow aluminum electrodes. The tube was operated at a uniform 50 cycle current of 40 ma, and at the following voltages:

Pressure in mm Hg	15.5	8.6	4.7	3.4	2.7	2.58
Voltage across tube	540	526	505	500	527	620

The helium used was purified by immersion in a charcoal, liquid-air trap for about 72 hours, then by circulation between two traps, one containing copper and copper-oxide at 300° to 400°C and the other containing charcoal at liquid-air temperature. The helium treated in this way showed no signs of impurities in its spectrum, except at the lowest pressure at which we worked (1.92 mm), where a few weak, unidentified lines appeared.

For photographing the spectra a replica concave grating of 1 meter focal length was used, in a Rowland mounting. Five horizontal reducers, constructed of Eastman neutral photographic filters, and transmitting approximately 100, 45, 20, 12 and 6 percent of the incident light, were mounted on the tangent to the focal circle at the plate, so as to cast a sharp horizontal image at the plate, in accordance with the astigmatism of the mounting. These reducers were calibrated in place by use of a vacuum thermocouple mounted at the camera to measure the transmitted energy at each wave-length.

The continuous comparison source was furnished by a tungsten ribbon filament, 2 by 35 mm, operated at 16 amperes. The temperature under these conditions was measured by Dr. C. H. Prescott[4] at the beginning and end of the work and was found to hold constant at 2014°K. From the known emissivity of tungsten,[5] relative values of the energy in various wave-lengths were calculated. For the weaker helium lines, where longer exposure times were necessary, the intensity of the continuous source was reduced throughout by narrowing the slit. No slit widths of less than 0.3 mm were used, however, in order that error due to diffraction might be avoided. The normal slit width was 1.5 mm.

The photographs thus obtained on Eastman panchromatic films, showing five spectra, of known relative intensities, side by side, were developed simultaneously in a tank arranged for constant stirring of the developer. The developer was elon-hydroquinone in standard Eastman proportions, and the best time of development was found to be six minutes, at room temperature. All subsequent operations of fixing and washing were carried out simultaneously for the two films.

The densities were determined by measurement, by a vacuum thermocouple, of the light transmitted through the exposed and clear films. Except in a very few cases, the Swartzschild formula was found to hold within three to five percent. Direct comparison with the continuous spectrum was used

[4] Prescott and Hincke, Phys. Rev. **31**, 130–134 (1928).
[5] Forsythe and Worthing, Astrophys. J. **61**, 146 (1925).

for all lines except for 3889, for which it was impractical to get a continuous source intense enough for comparison, and for the lines of the singlet sharp series, which were too faint for direct comparison. In these cases, the curves were compared with those of closely neighboring lines, and correction was made for sensitivity of the plate.

Fig. 1 shows a typical set of density-intensity curves illustrating both types of determination. The ordinates of density are the logarithms, to the base of ten, of the galvanometer deflection for the clear film divided by the deflection for the portion under consideration, while the abscissas are logarithms of the incident intensity through the various reducers. The horizontal distance between the curves for the continuous and helium films, then, gives the logarithm of the relative intensity for the two sources. The curve for 3889 was shifted to that for 4472.

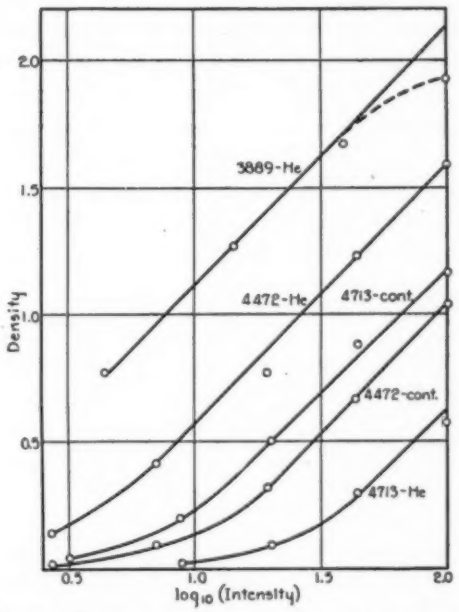

Fig.1. Typical set of density-intensity curves.

Absolute Intensities

Fig. 2 shows the results obtained for the absolute intensities of the thirteen lines studied (plotted on a logarithmic scale for convenience), the unit of intensity being taken arbitrarily as the light given at 5876A by the tungsten filament operating at 16 amperes, and with a slit width of 1.5 mm.

Since the error introduced by the irregularities in the photographic film determines the limits of accuracy, we may say that the probable error of any observation is not over five or six percent, for the more intense lines. The curves shown have, in general, been drawn within this limit of the observed points. A few points, notably those for 5876 at 12.1 and 20.0 mm pressure depart rather widely from the smooth curves. This, it seems, may be accounted for by the fact that this line was very near to the end of our films, where variations in emulsion, errors in development and the like would most probably enter to a large extent. For the six weakest lines, the parts of the density-exposure curves available were below the straight line portion, where best results were obtained, and we should estimate the probable errors on these to run somewhat higher, say eight to ten percent.

The trend of the curves toward a maximum at the lower pressures, with a subsequent decrease, is unmistakable. One of the interesting points in connection with this is the shift of this maximum to lower pressures as we go to higher members of the series, a rule which is violated in none of the cases.

Dr. I. S. Bowen has suggested that a possible explanation of these observed intensity variations may be found in the observation of Dymond[6] that the efficiency of excitation of a given initial state is greatest when the energy of the exciting electron is only slightly greater than that needed to excite that state. Consequently a given state with energy V_1 will be excited in most cases by electrons which have, at the time of impact, an energy between that necessary for excitation of this state and that of the next higher state, V_2.

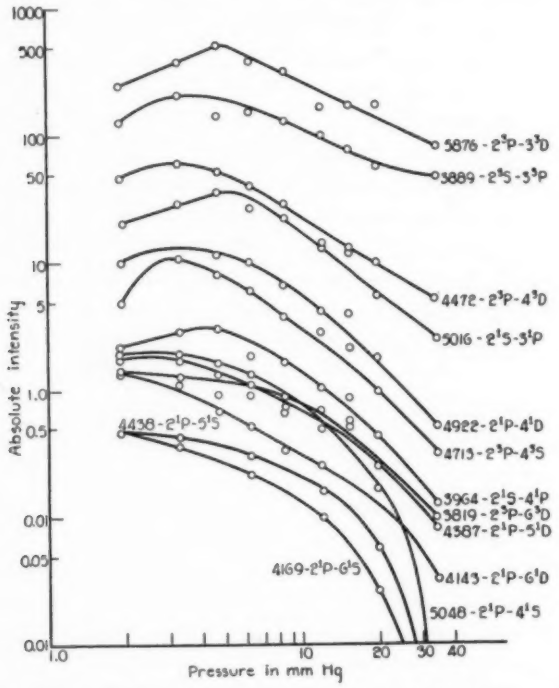

Fig. 2. Absolute intensities of thirteen lines of the helium spectrum.

Thus the probability of excitation of a given state is the same as the probability that an electron will have an impact when its energy is between V_1 and V_2. From the well known kinetic theory relations this probability is:

$$e^{-V_1/gy} - e^{-V_2/gy}$$

where g is the potential gradient in the tube and y is the electron mean free path.

Applications of this formula to the experimental data, while they do not agree quantitatively, do give the general type of curve obtained. The relative positions of the maxima, at least, are approximately correctly placed, although the slopes of the curves are much greater than for the experimental results.

Any exact solution of the mechanism of the variations, it seems, will require a greater knowledge of the variations caused by each factor: electron

[6] Dymond, Proc. Roy. Soc. A107, 291–309 (1925).

velocities, pressure, efficiency of impact and collisions of the second kind. With these objectives in mind, a program of work will be started in an attempt to throw more light on the phenomena.

If the sum of the intensities for all observed lines be taken, it is found that this follows a curve very similar to that for 5876, the maximum occurring at four millimeters, the point at which the resistance of the tube reaches a minimum of 12300 ohms, for the current used.

Relative Intensities

In Table I the values of the intensities of the various lines relative to 5876 and relative to the lowest observed member of the series are shown. While the regularities apparent in the absolute intensities are not nearly so marked in these values, certain general conclusions may be drawn:

(1) Within the pressure range in which we worked, decrease of pressure favors the singlet series with respect to the triplets.

(2) The higher members of the triplet series are decidedly favored by decrease of pressure, while the relative intensities within a given series of the singlet system shows a much smaller increase, except at the lowest pressure.

Table I. *Relative intensities of helium lines.*

Pressure in mm Hg		34.3	20.0	15.5	12.1*	8.6	6.3	4.7	3.3	1.92
Wave-length	Notation	Intensity Relative to 5876								
5876A	2^3P-3^3D	100	100	100	100	100	100	100	100	100
4472	2^3P-4^3D	6.20	5.89	7.52	8.48	9.2	10.6	10.4	15.8	18.8
3819	2^3P-6^3D	0.105	0.140	0.326	0.388	0.280	0.240	0.324	0.334	0.573
3889	2^3S-3^3P	57.8	32.0	45.2	58.5	40.8	40.0	28.4	54.0	51.0
4713	2^3P-4^3S	0.380	0.556	1.24	1.70	1.23	1.56	1.58	2.84	1.94
5016	2^3S-3^1P	3.06	3.18	6.84	7.95	6.96	6.93	7.08	7.50	8.23
		(100)	(100)	(100)	(100)	(100)	(100)	(100)	(100)	(100)
3964	2^3S-4^1P	0.155	0.245	0.558	0.504	0.528	0.487	0.605	0.739	0.885
		(5.05)	(7.7)	(8.2)	(6.3)	(7.6)	(7.0)	(8.6)	(9.8)	(10.7)
5048	2^1P-4^1S	—	0.110	—	0.289	—	0.346	—	0.492	0.768
			(100)		(100)		(100)		(100)	(100)
4438	2^1P-5^1S	—	0.033	—	0.099	—	0.078	—	0.111	0.174
			(30.3)		(34.0)		(22.5)		(22.6)	(22.7)
4169	2^1P-6^1S	—	0.015	—	0.063	—	0.058	—	0.094	0.183
			(13.8)		(21.8)		(16.0)		(19.1)	(22.8)
4922	2^1P-4^1D	0.620	1.01	2.28	2.45	2.06	2.59	2.26	3.33	4.03
		(100)	(100)	(100)	(100)	(100)	(100)	(100)	(100)	(100)
4387	2^1P-5^1D	0.010	0.095	0.287	0.394	0.230	0.284	0.265	0.450	0.695
		(16.1)	(9.4)	(12.6)	(16.1)	(11.0)	(11.0)	(11.3)	(13.5)	(17.2)
4143	2^1P-6^1D	0.004	0.07	0.143	0.195	0.165	0.176	0.209	0.287	0.562
		(6.45)	(6.93)	(6.28)	(7.95)	(8.0)	(6.8)	(9.2)	(8.8)	(13.9)

* Possibly all this column is high, because of probable error in 5876.

The authors wish to express their indebtedness to Dr. R. A. Millikan and to Dr. I. S. Bowen for their interest in the work and the help they have rendered us.

Norman Bridge Laboratory,
California Institute of Technology.
August 16, 1928.

SPECTRAL EXCITATION BY RECOMBINATION IN THE ELECTRIC ARC

By Jane M. Dewey[1]

Abstract

Recent measurements of electron velocities in arcs have made it probable that most of the light in the negative glow is emitted as a result of recombination of positive ions and electrons. Since the velocities of the positive ions are high, spectral lines emitted in this way should show Döppler broadening. This broadening was measured photometrically for a hot cathode arc in helium in which measurements of electron velocities were also made and results were obtained which can be explained by assuming all of the light in the negative glow to result from recombination of ions having a temperature about one-tenth that of the electrons.

RECENT investigations of electron densities and velocities in arcs have made it probable that spectra are emitted in the positive column of an arc principally as a result of direct excitation of atoms by electron collisions, but that in the negative glow the emission is mainly the result of recombination of positive ions and electrons. K. T. Compton suggested that, if this is the case, the lines emitted in the negative glow should show Döppler broadening corresponding to the known high velocities of the positive ions. Evidence of this broadening is presented here.

A hot cathode arc in helium was used in this investigation. The design of the arc is shown in Fig. 1. The cathode is of nickel, coated with barium oxide and heated by radiation from a tungsten spiral, and is operated at a barely visible red heat. These cathodes give a large electron emission at comparatively low temperatures and were supplied for this work by Dr. A. W. Hull of the General Electric Company, whose assistance is gratefully acknowledged. Two anodes are provided to permit striking a long arc with a positive column or a low voltage arc entirely within the bulb. The arc contains three exploring electrodes, one, two millimeters from the cathode and parallel to its upper surface, one, one centimeter from the cathode and in its axis (not shown in the figure) and one in the positive column opposite the window through which photographs of the light from the positive column were made. Currents of from a few tenths of an ampere to two amperes were put through the arc. The light intensity was very high in the negative glow as well as in the positive column, comparable to that in a small mercury arc. The negative glow, at pressures of less than a millimeter, is confined to a bright dome above the cathode and the light is sharply bounded, the remainder of the bulb being almost dark. The positive column starts sharply at the constriction and in these experiments always showed traces of striations, presumably due to the presence of hydrogen and neon as impurities, although neither of these impurities could be detected spectroscopically in exposures

[1] National Research Fellow.

long enough to show all the helium lines. The hydrogen lines were always visible when the arc was started but disappeared after a run of from a half-hour to an hour. A charcoal tube immersed in liquid air was always connected to the arc while it was running.

Typical data obtained by the method of Langmuir and Mott-Smith[2] are given for the arc in Table I. The concentrations and electron velocities in the negative glow are the results of averages for measurements with the two electrodes near the cathode. The space potential and electron temperatures were always the same within a few tenths of a volt and the difference in

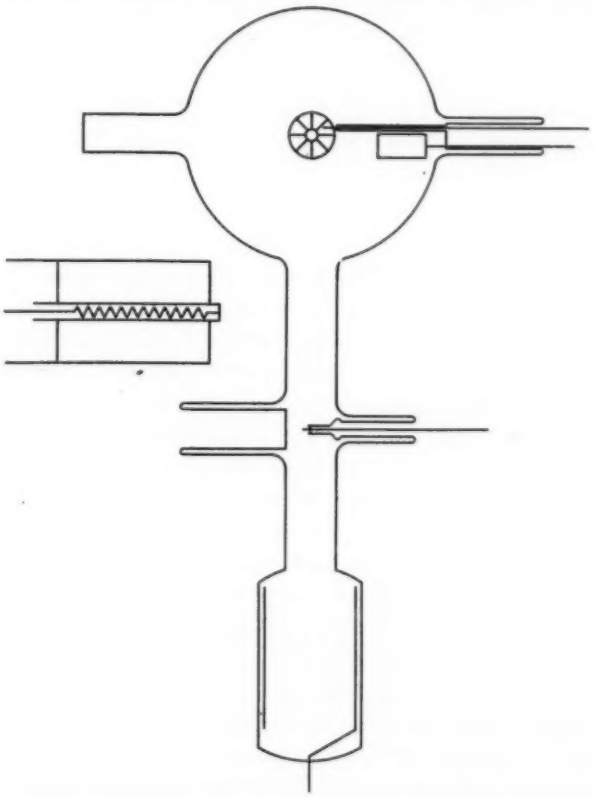

Fig. 1. Design of the arc and the cathode.

electron concentration was small and probably within the error of measurement. The difference in most probable electron velocities in the negative glow and in the positive column shows that a recombination spectrum is to be expected in the former case and an excitation spectrum in the latter, for in the negative glow only one collision of an atom with an electron in 10^8 takes place with the energy required to excite the helium spectrum while in the positive column the electron will have sufficient energy to excite in one collision in every three. On the other hand recombination takes place almost entirely by collision of slow electrons with positive ions. The calculated ratio

[2] Langmuir and Mott-Smith, Gen. Electric Review **27**, 449, 538, 616 (1924).

of the number of collisions of this type in which the electron has less than one-tenth volt energy is about 10^4 in the negative glow to one in the positive column. In making the measurements of line width the difference of electron concentration was exaggerated by using a smaller current during exposures in the positive column.

TABLE I. *Typical data for the arc as obtained by the method of Langmuir and Mott-Smith.*

Potential (volts)	Current (amp.)	Pressure (mm)	Electron concentration		Electron temperature		Cathode fall (volts)
			Negative glow (Electrons per cc)	Positive column (Electrons per cc)	Negative glow (volts)	Positive column (volts)	
92	1.6	1.2	2.5×10^{12}	4.1×10^{11}	0.74	3.4	35
93	1.7	0.9	1.4×10^{12}	3.8×10^{11}	0.96	4.9	36
104	0.36	0.5	7.0×10^{11}	9.1×10^{10}	0.52	5.5	34
39	2.0	0.4	3.2×10^{12}	short arc	0.88		
55	1.9	0.25	1.7×10^{12}	short arc	0.88		

Measurements of line width were made with a Lummer-Gehrcke plate of resolving power about 250,000. Blackening was measured in a microphotometer and the relation between intensity and blackening established by varying the time of exposure.[3] Hammer orthochromatic plates were used for the green lines, and Eastman extreme red sensitive plates for the lines 6678 and 7281. All plates were developed for four minutes at 17° in Rodinal, one part to twenty parts water. The exposure times varied from two minutes for 5016 to two hours for 7281. It was unfortunately not possible with the Lummer-Gehrcke plate available to make measurements on the orthohelium spectrum as the spectral range of the plate results in exact superposition of the "doublet" components. The lines measured were chosen for small and varying Stark effect. The data are given in Table II. Line width refers to the difference in Angstroms between the two points at which the line has one-half its maximum intensity. All but three of the measurements are averaged from two or more exposures. With the exception of one at a pressure of 0.25 millimeters of mercury all were made on the long arc. Unfortunately the correction for the instrumental width of the lines is large enough to introduce some uncertainty. The difference between the width of a line emitted in the positive column and one emitted in the negative glow is nearly independent of this correction, however. The width of the lines increases regularly with increasing wave-length, as is to be expected of a Döppler broadening. The Stark effect broadening would vary irregularly with wave-length, with 7281 as the narrowest of the lines measured. More striking evidence that the width of the lines in the negative glow is due to the high velocities of the positive ions is the regular decrease in line width with increasing pressure shown for the line 5016. Since the positive ions are dissipating energy by collision with atoms of the gas this is to be expected if they are the emitters, but on no other basis. This decrease shows that the broadening is not merely ap-

[3] That this method does not introduce appreciable errors under these conditions has been shown by the author, Phys. Rev. 30, 774 (1927).

TABLE II. *Data on the Döppler broadening of helium lines.*

Portion of Arc	Line	Pressure (mm)	Electron concentration (Electrons per cc)	Width observed corrected	Electron temperature* (volts)	Temperature of emitter*
Negative glow	$2P-3S$, 7281A	0.4	2.1×10^{12}	0.133A 0.11A	1.2	0.16V
Positive column	$2P-3S$, 7281	0.4	8.0×10^{10}	0.091 0.07	6.2	500°K
Negative glow	$2P-3D$, 6678	0.4	2.1×10^{12}	0.111 0.09	1.2	0.12V
Positive column	$2P-3D$, 6678	0.4	8.0×10^{10}	0.080 0.06	6.2	500°K
Negative glow	$2P-4S$, 5047	0.4	3.4×10^{12}	0.079 0.06	0.87	0.11V
Positive column	$2P-4S$, 5047	0.4	1.1×10^{11}	0.054 0.04	5.5	500°K
Negative glow	$2S-3P$, 5016	0.25	1.8×10^{12}	0.086 0.07	0.86	0.14V
		0.4	3.4×10^{12}	0.072 0.06	0.87	0.09V
		0.5	7.5×10^{11}	0.075 0.06	0.52	0.10V
		1.1	3.2×10^{12}	0.066 0.05	0.66	0.07V
Positive column	$2S-3P$, 5016	0.4	1.6×10^{11}	0.046 0.03	5.5	350°K
		0.5	9.6×10^{10}	0.050 0.04	5.5	400°K

* 1 volt = 11,600°K.

parent and due to self-reversal, as the reversal would increase with increasing pressure. Any explanation based on absorption by excited atoms is, furthermore, excluded by the regularity of broadening as a function of wavelength.

When this investigation was begun it was thought from the measurements of Langmuir and Mott-Smith[2] that positive ions had energies as high as one-half the electron energies. Since then Langmuir, from consideration of what occurs in the vicinity of an exploring electrode in a gas, has come to the conclusion that the large apparent velocities of the positive ions in his measurements in mercury arcs are due to the field set up by the exploring electrode itself and not to the existence of ions of these volocities in the body of the gas. Since Dempster[4] and Harnwell[5] have shown that positive ions dissipate energy much less rapidly than we should expect on a mechanical basis it is to be expected that they will have velocities considerably higher than the velocities of the neutral atoms. The last column of Table II gives the temperature of the emitter on the assumption that the total corrected width of the line is due to Döppler broadening and that there is a Maxwellian distribution of velocities of emitters. This latter assumption is borne out by the form of the intensity curves of the lines, whose intensity drops off rapidly outside the half-width. This shows that lines are not emitted in the negative glow partly as a result of direct excitation and partly by recombination of ions having a temperature higher than that calculated from the half-width. A few measurements were made of the variation of the intensity of the light in the negative glow with varying electron concentration. The light intensity increases approximately as the square of the electron concentration, confirming the conclusion that the glow is due principally to recombination. The negative glow of a hot cathode arc thus affords a source of light of known excitation.

I wish to thank Professor K. T. Compton for many suggestions on the design of the arc as well as for the general method of attack on the problem.

PALMER LABORATORY,
PRINCETON, N. J.
September 11, 1928.

[4] Dempster, Phil. Mag. **3**, 115 (1927).
[5] Harnwell, Phys. Rev. **31**, 634 (1928).

SECONDARY ELECTRON EMISSION PRODUCED BY POSITIVE CAESIUM IONS

By J. M. Hyatt

Abstract

Number of electrons emitted from a Cs covered grid and plate per positive Cs ion striking them.—The source of the positive caesium ions, a short tungsten filament maintained at about 1200°K in the presence of caesium vapor, was mounted on the axis of a long cylindrical grid and plate. The plate current and total positive ion emission current were observed for each of several negative grid potentials as the plate potential was varied from +50 to −650 volts. From these observations the number of electrons that were emitted from the caesium covered grid and plate per positive ion was calculated. This number increased uniformly from 0.01 at approximately 100 volts to 0.15 at 600 volts.

Calibration of tube.—After corrections for the emission of secondary electrons were made, the ratio of the positive ion current to the plate to the total emission current was found to be independent of the plate and grid potentials for plate potentials greater than 0.2 of the grid potential. This ratio, 0.72, is the same as the ratio between the total area of the plate less the projected area of the grid, and the total plate area. Assuming the same distribution of electrons as positive ions, we can calculate the ratio of the plate current to the grid current in this type of tube.

Introduction

THE subject of secondary electron emission from various surfaces due to the bombardment of positive ions has been investigated by several people.[1–4] Similar studies have recently been made by Klein[5] and Jackson.[6]

The material presented in this paper describes experiments with a three-electrode tube to determine the number of electrons emitted from a caesium covered molybdenum surface per caesium positive ion as a function of the accelerating potential.

Apparatus

A diagram of the tube and electrical connections is shown in Fig. 1. The source of the positive ions was a tungsten filament, *F*, 2.5 cm long maintained at about 1200°K in the presence of caesium vapor.[7] This filament was mounted along the axis of a cylindrical grid, *G*, 4.5 cm long made of 0.0127 cm (5 mil) molybdenum wire wound on a 0.75 cm mandrel. There were forty turns of grid wire per 2.5 cm length of grid. A cylindrical molybdenum plate, *P*, 1.3 cm in diameter and 4.5 cm long, was mounted outside the grid and

[1] Cheney, Phys. Rev. **10**, 335 (1917).
[2] Baerwald, Ann. d. Physik **41**, 643 (1913); **60**, 1 (1919); **65**, 167 (1921).
[3] Hahn, Zeits. f. Physik **14**, 355 (1923).
[4] Baderau, Phys. Zeits. **25**, 137 (1924).
[5] Klein, Phys. Rev. **26**, 800 (1925).
[6] Jackson, Phys. Rev. **28**, 524 (1927); **30**, 473 (1927).
[7] Langmuir and Kingdon, Science **57**, 58 (1923).

coaxial with it. These electrodes were mounted in a lime glass tube with a side tube from which the caesium was to be distilled. The tube was evacuated by a mercury vapor pump backed by an oil pump. A trap was immersed in liquid air during the exhaust. The tube was baked out at about 200°C while the pumps were running. A higher temperature bakeout resulted in leakage currents across the stem after the caesium had been distilled into the tube.

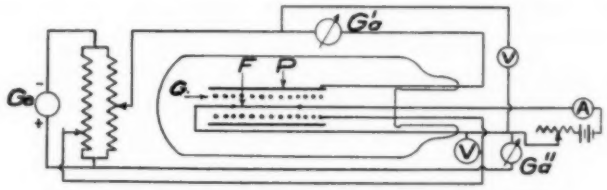

Fig. 1. Diagram of tube and electrical connections.

The filament was held at a high temperature for several seconds to free it of absorbed gases. The plate and grid were heated by induction until all evidence of emitted gases had disappeared.

Caesium was formed in the side tube by heating a mixture of caesium chloride and calcium. The caesium was then distilled into the tube and the side tube drawn off. The experimental tube was then sealed off from the pumping system and tested.

The filament was heated by the current from a storage battery and the grid and plate potentials were maintained by a motor generator set, *Ge*. The positive ion emission from the filament which was approximately two microamperes at the existing caesium vapor pressure was measured by a galvanometer, *Ga''*. A galvanometer, *Ga'*, in the filament-plate circuit indicated the net current to the plate.

Experimental Procedure

The experiments were carried on while the tube was immersed in a water bath maintained at 20°C in order to hold the pressure of the caesium vapor constant. The grid and plate were, of course, covered with at least a monatomic layer of caesium throughout the experiments.

The positive ion emission from the filament and the plate current were observed as the plate potential was varied from +50 to −650 volts with respect to the positive end of the filament, while the grid potential was maintained constant at each of several values between −100 and −600 volts.

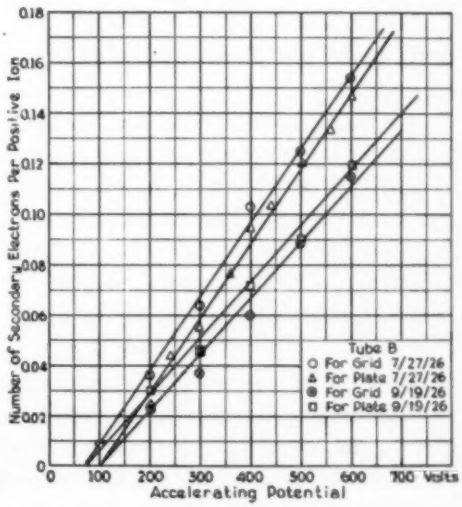

Fig. 2. Secondary electron emission produced at the grid and plate by caesium positive ions. Tube B.

Results

The number of secondary electrons produced by the impact of positive ions on the grid may be found as follows: While the plate potential was being varied from +50 to 0, the plate current was constant and consisted of electrons which were emitted from the caesium covered grid by the bombardment of positive ions. This is shown by the points below the abscissa axis in Fig. 4. At these plate potentials all positive ions were collected by the grid. The electron current to the plate divided by the positive ion current from the filament gives the number of secondary electrons per positive ion on the grid. This ratio for various accelerating grid potentials is shown by the curves for the grid in Fig. 2.

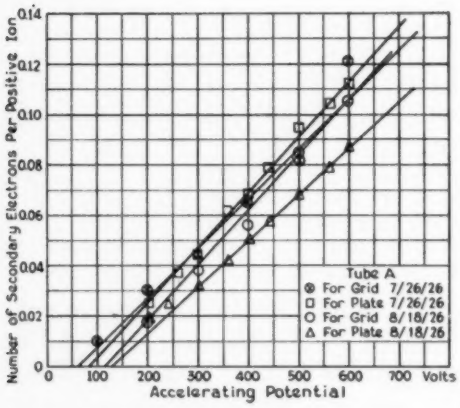

Fig. 3. Secondary electron emission produced at the grid and plate by caesium positive ions. Tube A.

The number of secondary electrons per positive ion increases uniformly from 0.01 at 100 volts to about 0.15 at 600 volts. The second curve for the gird was plotted from data taken at a later date and it shows that the ratio of secondary electrons to positive ions is less than indicated by the first curve. This difference is due to a change in the surface condition of the caesium. The curves for the grid that are shown in Fig. 3, were plotted from the data taken, with a second tube. A comparison of the two sets of curves shows that the secondary emission starts at about 100 volts in both cases but that the increase with accelerating potential is less for the second tube.

As the plate potential was made negative for a fixed negative grid potential, the plate current reversed because the plate began to collect positive ions in addition to the electrons from the grid. This condition is shown by the curve in Fig. 4. The ordinates represent the plate current, I_p, and the abscissas represent the plate potential, E_p. The potential of the grid was maintained at -500 volts. I_p rapidly attains a value which is quite constant between the values of E_p, -50 and -500. Immediately below the value of E_p equal to 500 volts, there is a rapid increase in I_p. This is followed by a nearly uniform increase in I_p as E_p increases.

The nearly horizontal portion of the curve in Fig. 4 indicates that for a given grid potential the plate current, which is made up of positive ions from the filament and secondary electrons from the grid, is constant until the plate becomes as negative as the grid. As the ratio of plate to grid voltage passes through unity, the plate ceases to collect secondary electrons from the grid and begins to lose them to the grid. The increase in I_p as the plate is made

more negative than the grid indicates that the number of secondary electrons from the plate increases as the positive ion speed increases.

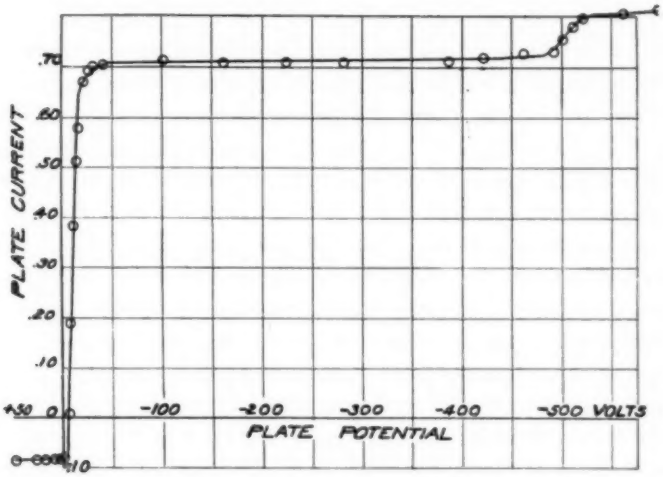

Fig. 4. Total plate current as a function of plate voltage with the grid at −500 volts. Positive ordinates indicate an excess of positive ions to the plate, negative ordinates indicate an electron current from grid to the plate.

In order to analyze the type of data shown in Fig. 4, the ratio of the plate current, I_p, to the total emission current I_0, is plotted as ordinates, and the ratio of the plate potential, E_p, to the grid potential, E_g, is plotted as ab-

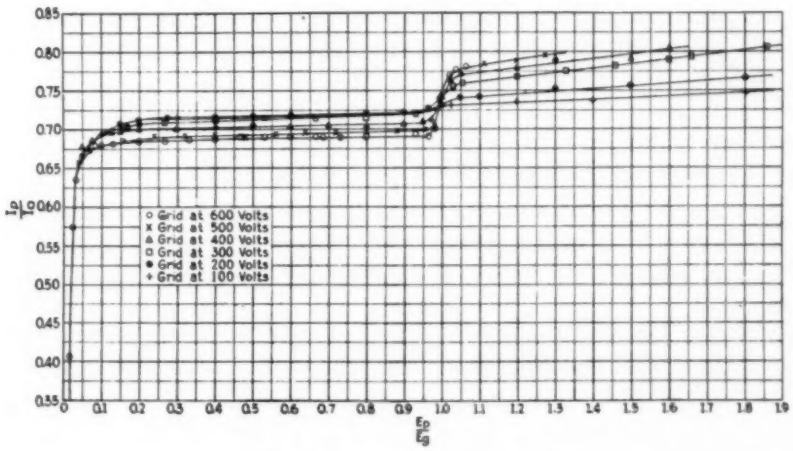

Fig. 5. Curves showing the ratio of the plate current, I_p to the emission current, I_e, as a function of the ratio of the plate potential, E_p, to the grid potential, E_g.

scissas in Fig. 5 for each of several grid potentials. The values of I_p/I_0, for each grid potential, rapidly attains a value which is constant between the

values of E_p/E_g 0.2 and 1. For values of E_p/E_g greater than 1 there is a nearly uniform increase in I_p/I_0.

Fraction of Positive Ions Striking Grid and Plate

In order to calculate the number of secondary electrons that are emitted from the plate per positive ion, it is necessary to know the actual primary positive ion current to the plate. This current may be calculated from the data in Figs. 2 and 5 as follows. Consider, in Fig. 5, the portion of the 600 volt curve between E_p/E_g equal to 0.2 and 0.95. The difference between the ordinate 1 and the average value of I_p/I_0 for that part of the curve represents the fraction of the total current that reaches the grid. This grid current is made up of positive ions from the filament and secondary electrons from the grid itself. If the value of the grid current be multiplied by the value of the number of secondary electrons per positive ion at the grid obtained in Fig. 2, the result approximately represents the secondary electron current from grid to plate. This value is a little too large, since the grid current included the secondary electrons emitted to the plate. However, if the calculated value of the secondary electron current from the grid be added to the observed plate current, we obtain an approximate value of the actual positive ion current to the plate. This current is a little too large because the value of the grid current with which we have started is a little too large. If the calculation is again made, using the new value of the plate current, calculated as described above, we obtain a value of the positive ion current to the plate which is probably very near the true current. This current, which is in terms of unit emission from the filament, represents the fraction of the positive ions striking the plate for the given value of the grid potential.

If the same calculation is applied to the curves in Fig. 5, for each grid potential, the resulting values of the ratio I_p/I_0 do not differ by more than one percent from their mean, which is 0.724. This indicates, at least for grid potentials between 100 and 600 volts, that the relative distribution of positive ions between grid and plate is constant as long as the potential of the plate is greater than 0.2 and less than 0.95 of the grid potential.

It is probable that this same distribution of positive ions holds for ratios of E_p/E_g greater than unity. If this distribution is assumed, then, in Fig. 5, the difference between the values of I_p/I_0 and 0.724, above E_p/E_g equal to 1, is represented by the secondary electron current emitted from the caesium covered plate. This difference for a given E_p divided by 0.724 gives the number of secondary electrons per positive ion incident on the plate.

It was found that these ratios of secondary electrons to positive ions for a given plate potential but for the different grid potentials were in agreement, and were also in agreement with the number of secondary electrons per positive ion for the grid. This justifies the assumption made above that the fraction of positive ions which goes to grid and plate respectively, is constant for all values of E_p/E_g; the plate collecting 72 percent and the grid 28 percent of the ions emitted from the filament.

The curves for the plate that are shown in Fig. 2, were plotted from the results calculated in this way. The number of secondary electrons per positive ion increases uniformly from 0.01 at 100 volts to 0.15 at 600 volts. The two curves for the plate were plotted from data taken with an interval of six weeks. The difference between them indicates a change in surface conditions.

The curves in Fig. 3 show the relation between the number of secondary electrons per positive ion and the accelerating potential for the caesium covered plate in a second tube.

Calibration of Tube

The plot shown in Fig. 6, represents the fraction, F, of the total ion emission that reaches the plate as a function of E_p/E_g after the secondary electron emission from the grid and plate has been taken into account for each of the curves in Fig. 5. The actual positive ion current to the plate per unit ion emission from the filament for each of the grid potentials lie within the shaded region of the plot, and the average 0.725 is represented by the horizontal line.

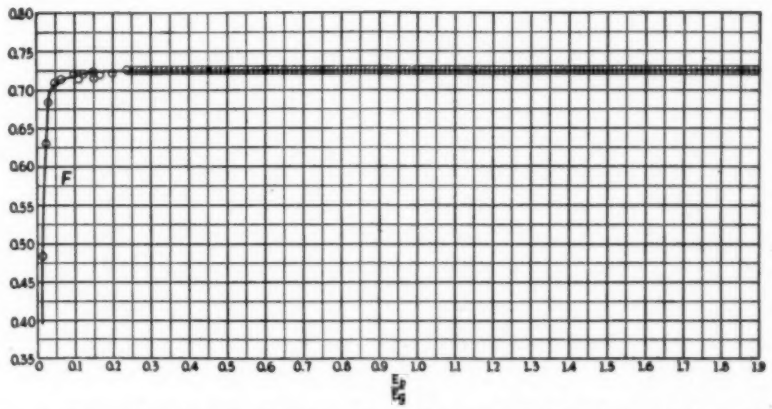

Fig. 6. Curve showing the fraction, F, of the total positive ion emission that reaches the plate as a function of the ratio E_p/E_g.

Upon referring to Fig. 2 again, it may be observed, according to the intercept on the abscissa axis, that the secondary emission from the grid at accelerating potentials less than 100 volts is zero. Observations that were made when both the plate and grid were maintained at -50 volts showed that the ratio, I_p/I_0, was 0.723, a value close to the corresponding one found above.

It was anticipated that the fraction of positive ions caught by the grid and plate respectively, would be the same as the ratio of solid to open portions of the grid. Accordingly, the area of the inner surface of the plate and the projected area of the grid on the plate per centimeter length of the plate were calculated from their dimensions. The ratio of the projected grid area to the total plate area turns out to be 0.27 and the ratio of the plate area less the projected grid area to the total plate area is 0.73. This last ratio is very close to the ratio 0.725, shown in Fig. 6. It can be shown theoretically that the

paths of positive ions in a tube of this type are the same as those of electrons at the same accelerating voltage. Hence it may be assumed that with positive voltages of grid and plate the fraction of electrons caught by the grid will be measured by the projected area of the grid. This result is of considerable importance for work on secondary electron emission. It obviously applies, so far as the present evidence goes, only to cylindrical tubes of the type used in these tests.

The writer wishes to express his gratitude to Dr. A W. Hull for his many helpful suggestions and criticisms during the course of this investigation.

RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY,
SCHENECTADY, NEW YORK.
September 13, 1928.

SECONDARY ELECTRON EMISSION FROM MOLYBDENUM

By J. M. Hyatt and H. A. Smith

Abstract

The secondary electron emission from a very clean molybdenum plate in a simple three-electrode tube has been studied. The number of primary electrons striking the plate was calculated by means of the positive ion calibration method previously reported. The number of secondary electrons per primary reaches a maximum value of 1.15 at 600 volts and then decreases to 1.00 at 2000 volts. One definite discontinuity in the secondary emission curve occurs at 13.5 volts; the others are very small and are not reproducible. The emission increases about 3 percent within a few minutes after heating if the gas pressure is very low and then remains quite constant for a long period of time. The emission decreases with time when there is more gas present. The secondary emission appears to increase by about 4 percent when the temperature of the target increases from the normal operating temperature to 1600°K.

Introduction

THE emission of electrons from metal surfaces due to electron bombardment has been investigated by several observers [1–13] in the past few years. Petry[14] has reported on the secondary emission from molybdenum, and has shown that discontinuities occur at several accelerating potentials in the secondary emission curve. The object of the present investigation has been to study the secondary emission from an exceptionally clean molybdenum plate by using a simple type of three electrode tube that had been calibrated by the caesium positive ion method reported by one of the authors.[15]

Apparatus and Procedure

The electrodes were removed from the bulb used in the calibration experiment and mounted in a Pyrex glass bulb, shown in Fig. 1, in order to permit a higher temperature during the oven bake-out.

[1] A. W. Hull, Phys. Rev. **7**, 1 and 141 (1916).
[2] H. M. Dadourian, Phys. Rev. **14**, 434 (1919).
[3] Horton and Davies, Proc. Roy. Soc. **A97**, 23 (1920); Phil. Mag. **46**, 129 (1923); **47**, 245 (1924).
[4] I. G. Barber, Phys. Rev. **17**, 332 (1921).
[5] Millikan and Barber, Proc. Nat. Acad. Sci. **7**, 13 (1921).
[6] J. T. Tate, Phys. Rev. **17**, 394 (1921).
[7] Davisson and Kunsman, Phys. Rev. **19**, 253 (1922).
[8] H. E. Farnsworth, Phys. Rev. **20**, 358 (1922); **25**, 41 (1925); **27**, 413 (1926); **31**, 405 (1928); **31**, 414 (1928); **31**, 419 (1928).
[9] E. W. B. Gill, Phil. Mag. **45**, 864 (1923); **46**, 994 (1923).
[10] L. E. McAllister, Phys. Rev. **21**, 122 (1923).
[11] O. Stuhlman, Phys. Rev. **25**, 234 (1925).
[12] H. E. Krefft, Phys. Rev. **29**, 908 (1927).
[13] J. B. Brinsmade, Phys. Rev. **30**, 494 (1927).
[14] R. L. Petry, Phys. Rev. **26**, 346 (1925).
[15] J. M. Hyatt, Phys. Rev. **32**, 922 (1928).

The source of the primary electrons was a straight tungsten filament, *F*, 0.0178 cm (7 mil) in diameter and 2.5 cm long. This filament was mounted on the axis of a cylindrical grid, *G*, 0.76 cm in diameter and 4.45 cm long. The grid was made of 0.0127 cm (5 mil) molybdenum wire wound in a spiral with 40 turns per 2.5 cm, and was supported by four molybdenum wires, 0.0508 cm (20 mil) in diameter. The cylindrical plate, *P*, which was mounted coaxial with the grid, was 1.27 cm in diameter and 4.45 cm long.

The tube was exhausted by means of a two stage condensation pump backed by an oil pump and then baked out at 450°C for two hours. The filament was flashed and the grid cleaned up by electron bombardment. The plate was then heated by induction to a temperature of 1600°K as measured by a calibrated tungsten filament. The heat treatment of the plate continued until there was no trace of gas evolved during heating, as indicated by the sticking of the mercury column to the top of the McLeod gauge. The tube was then sealed off the pump and tested.

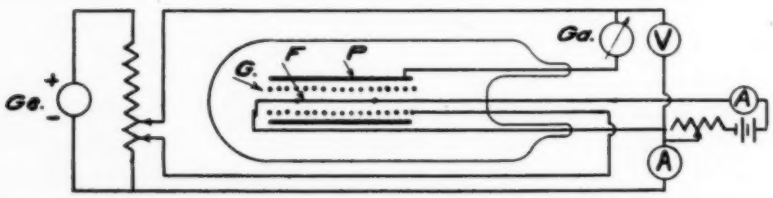

Fig. 1. Diagram of tube and electrical connections.

While the observations were being made, the tube was immersed in liquid air contained in an unsilvered vacuum flask, which was surrounded by the coil of a high frequency induction furnace. This enabled the plate to be heated while the tube was immersed in liquid air.

A diagram of the electrical connections is shown in Fig. 1. The filament was heated by the current from a storage battery and the electron emission from it was measured by a milliameter, *A*, (1 m.a. full scale). The grid and plate potentials were supplied by means of motor generator sets, *Ge*, that were found to be remarkably steady. During all of the experiments, the potentials of the grid and plate were maintained positive with respect to the filament. The grid potential was always at a value 4/3 that of the plate to ensure that the grid collected all the secondary electrons emitted by the plate. A galvanometer, *Ga*, in the plate-filament circuit served to measure the plate current. The electron emission from the filament was maintained at about one milliampere to give the same space charge effect as was produced by the positive ion current of 2 microamperes in the positive ion calibration previously reported. This current was calculated from the relative masses of the caesium ion and the electron.

Before any observations were recorded, the plate was heated to about 1600°K while the tube was immersed in liquid air. The plate current was then observed for a plate potential of 350 volts and it was found that the current became quite steady after the furnace had been turned off for 2

minutes. The plate was repeatedly heated at intervals until the same value of the plate current was found at the end of each of several heatings.

In order to determine the number of secondary electrons per primary for the plate as a function of the accelerating potential the following experimental procedure was adopted. The plate potential was set at a given value and the grid potential was made 4/3 of it. The temperature of the filament was adjusted to give 1 milliampere emission. Then, while the filament current was on but the plate and grid potentials off, the plate was heated to about 1600°K for 1 min. The plate and grid voltages were applied and at the end of 3 min. the emission and plate currents were observed. This was repeated for increasingly greater accelerating potentials up to 2000 volts. At the end of a run the plate current was again observed for the plate potential of 350 volts. If the current did not check its initial value to within one percent the data were discarded.

This run was repeated with the tube four times, two of them were made after the tube had been opened up and re-exhausted each time. The degree of vacuum differed some in the five determinations, but tests using the tube as an ionization gauge indicated that the pressure was lower than 10^{-7} mm Hg.

We are assuming that the electron current is divided between the grid and plate in the same ratio that the positive ion current was found to be distributed as previously reported.[15] Taking 0.724 milliamperes as the primary electron current to the plate for an emission current of 1 milliampere, we find the secondary electron current by subtracting the observed plate current from 0.724, or by adding it to 0.724 if the plate is losing more secondary electrons than it is receiving primary. This secondary current divided by 0.724 gives the number of secondary electrons per primary electron at the plate.

Results

The curve in Fig. 2 shows the number, n, of secondary electrons, I_s, per primary, I_p, as a function of the accelerating potential, that was calculated from observations made under the best vacuum conditions that we had. There was no measurable trace of gas present in the tube during the run. The maximum value of n for molybdenum, 1.25, reported by Petry[14] is comparable with our value but it occurs at about 360 volts instead of about 600 volts as Fig. 2 shows. Points calculated from data taken in various other runs are also shown in the figure. The amount of gas present in the tube before it was immersed in the liquid air was slightly different in each case. The general shape of the curves is the same, but the secondary emission is less when the gas in the tube has not been cleaned up so well.

In order to determine whether there were any discontinuities in the secondary emission curve, observations were made with a commutator in the circuit to turn off the filament current while the grid and plate potentials were applied. This insured an equipotential surface over the cathode. The plate had been heated thoroughly and the tube was immersed in liquid air. Readings of the emission and plate currents were made at intervals of 1 volt for the accelerating potentials. The run was not completed in one day but was pieced

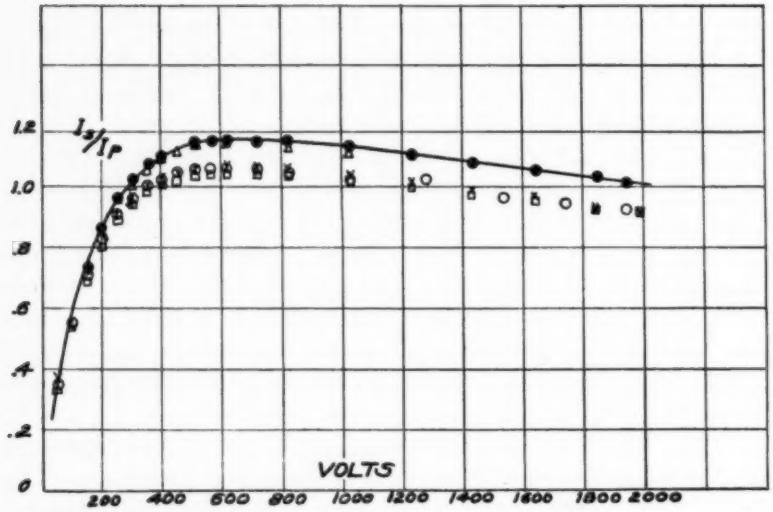

Fig. 2. Number of secondary electrons per primary as a function of the accelerating potential. Run 1, marked with circles, was taken when the tube contained a slight amount of gas before immersion in liquid air. Run 2, marked with squares, was taken when the tube contained slightly more gas than in Run 1. The tube was immersed in liquid air. Run 3, marked with crosses, was taken after the tube had been re-exhausted. The tube was immersed in liquid air. Run 4, marked with triangles, was taken after the tube had again been re-exhausted, with the tube on the pump and not immersed in liquid air. Run 5, the curve marked with black circles, was taken after the tube had been withdrawn from the pump and immersed in liquid air. No measurable trace of gas was found at the end of the run.

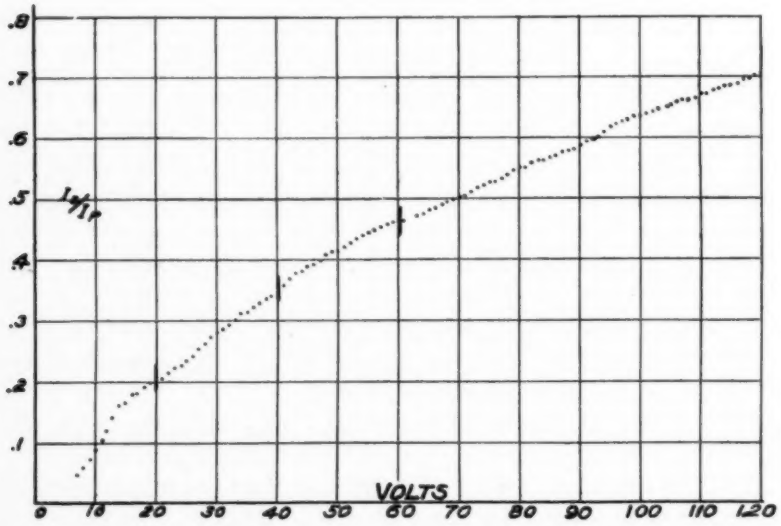

Fig. 3. Secondary emission data taken with equipotential cathode and at 1 volt steps. The parts of the curve between the vertical dividing lines were taken at different times.

together from data taken on several days; care being taken that former observations were checked by the new ones. However, in spite of these precautions, there are discontinuities where the data overlap. Fig. 3 shows that there is only one outstanding break which comes at 13.5 volts. The other small changes in the slope are probably of the same order as the experimental errors. The break at 13.5 volts was reproduced in different runs, but the others were not. Even though the surface was as free of gas as it is probably possible to make it and the vacuum conditions the best obtainable, it does not seem worth while to attach any significance to the breaks in the curve.

Change in I_s/I_p With Time

It was observed that the plate current changed with time after the plate had been heated to a bright red heat. After the data shown in Fig. 2 had been obtained, the plate was heated to about 1600°K for one minute and then the plate and emission currents were recorded at the end of definite time intervals for an accelerating potential of 350 volts. The calculated values of I_s/I_p are

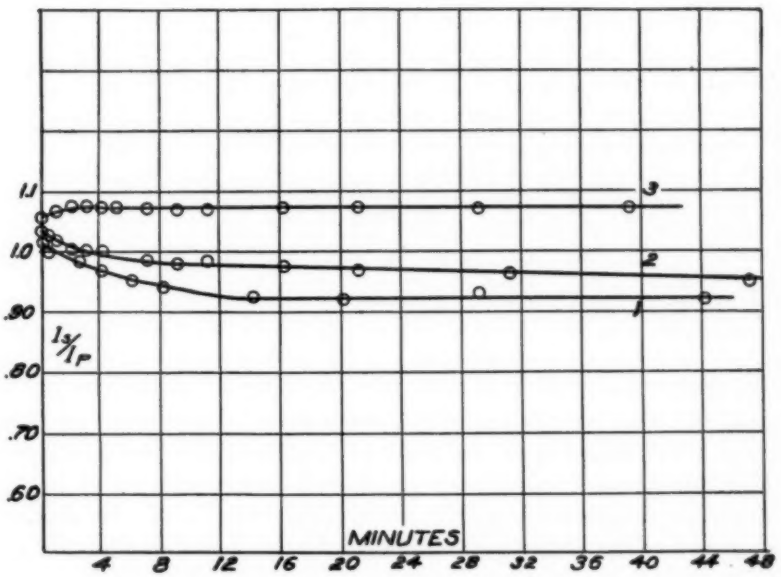

Fig. 4. Change in secondary emission with time after the plate started to cool. Curve 1 was taken immediately after Run 2, Fig. 2; curve 2, after Run 3, Fig. 2; curve 3, after Run 5, Fig. 2.

plotted in Fig. 4. The change in I_s/I_p was probably due to the re-absorption of gas on the plate. When there was a small measurable trace of gas present, I_s/I_p decreased with time and the more gas present, the more rapid the decrease. When there was no measurable trace of gas present, the ratio increased slightly for the first 2 minutes and then remained constant for a period of 40 minutes.

Change of Secondary Emission with Temperature

It was found possible to make determinations of secondary emission while the plate was being heated to incandescence by the high frequency furnace. The tube circuits present a high impedance to the radio frequencies at which the furnace operates. When the furnace was turned on and off, no change in the reading of the instruments could be detected before the plate had time to change appreciably in temperature. With the tube immersed in liquid air, the emission and plate currents were observed at 20 sec. intervals from the instant the furnace was turned on. The plate reached its equilibrium temperature of approximately 1600°K in about 30 sec. The calculated I_s/I_p ratio is shown in Fig. 5, curve 1. The data shown in curve 2 were obtained a few minutes after the completion of the first run.

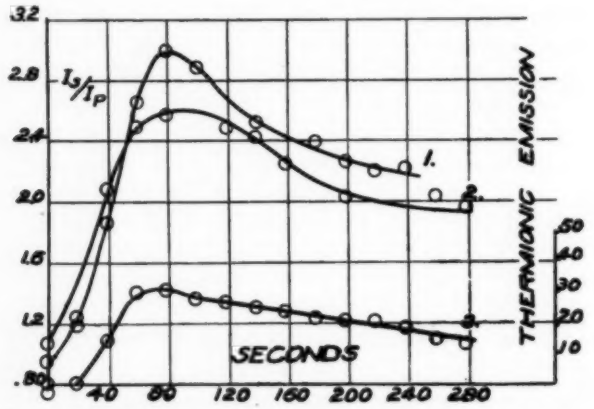

Fig. 5. Curves 1 and 2, secondary emission from plate while being heated; curve 3, thermionic current from plate while being heated with filament cold.

It seemed probable that thermions as well as secondary electrons were being liberated from the plate at this temperature. While the plate was being heated with the filament cold, the plate current was observed as a function of time. This thermionic current from the plate is shown in curve 3, Fig. 5. It is significant that the maximum of the curve coincides with the maximum of the I_s/I_p curve. The change with time must be due to driving off the absorbed gas from the plate.

In order to correct the observed current for the thermionic emission from the heated molybdenum plate, the following experiment was performed. After the plate had been thoroughly heated and cooled to its equilibrium temperature I_s/I_p was determined. The plate was then heated to incandescence for several minutes until a steady value of the plate current was obtained. This plate current and the corresponding emission current were recorded. Then, without turning off the furnace, the filament current was turned off, and the thermions that were liberated from the plate were collected by the grid; since the grid potential was 4/3 that of the plate. The former plate current, obtained with the filament heated, was then corrected for the

thermions from the plate. The results of this determination for an accelerating potential of 300 volts give values of I_s/I_p for the cold plate of 1.10 and for the hot plate of 1.14. This shows a change of 3.6 percent in the secondary emission and, if the surface could be entirely cleaned, the indications are, that the change would be zero.

The writers are pleased to acknowledge their indebtedness to Dr. A. W. Hull for his advice and encouragement during the progress of the experiments.

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SCHENECTADY, N. Y.
September 13, 1928.

THE IONIZATION OF CARBON MONOXIDE BY CONTROLLED ELECTRON IMPACT, INTERPRETED BY THE MASS SPECTROGRAPH

By T. R. Hogness and R. W. Harkness

Abstract

By using a mass spectrograph previously described, a study is made of the ionization processes occurring when CO molecules are ionized by electrons of definite energy. The variation of the relative intensities of the ions CO^+, C^+ and O^+ with changes of pressure and with changes of the electric fields has led to the conclusion that the principal procesess occurring are: (1) $CO = CO^+ + E^-$; (2) $CO = O^+ + C + E^-$; (3) $CO = C^+ + O + E^-$; (4) $CO + CO^+ = CO_2 + C^+$. No negative nor doubly charged positive ions were found.

IN THE many studies of ionization processes[1] that have been made with the mass spectrograph, it has been found that dissociation of a gas molecule may accompany the ionization process. The dissociation of the ionized molecule into an ion and an atom or radical can take place in two ways: (1) the dissociation may be simultaneous with the ionization by electron impact; or, (2) the dissociation may result from the secondary collision of the ionized molecule with a neutral one.

The first of these dissociation processes can be explained quite satisfactorily by the same reasoning as adopted by Franck[2] in explaining dissociation by light absorption. The mechanism of the latter process, dissociation by collision, is, however, yet somewhat uncertain. The best example of this latter process is the ionization of nitrogen.[3] Only N_2^+ ions are formed by the electron impact. Those of the N_2^+ ions which possess 24 or more volts energy dissociate upon collision with gas molecules. Whether the collision produces a rearrangement of the electron system of the N_2^+ ion, such that it is unstable with respect to N^+ and N, or whether the impact of the collision results in added vibrational and rotational energy sufficient to dissociate the N_2^+ ion, has not been decided. The existing band spectral knowledge of this gas does not help us here. With the view of obtaining more data on this phenomenon, we chose to study the ionization processes of carbon monoxide. Carbon monoxide more nearly resembles nitrogen than any other gas. In its physical properties, it is very similar to nitrogen in that both gas molecules have the same total number of electrons, similar band spectra and very probably similar electron structures.

It might then be expected that these two gases should have similar ionization processes. Unlike nitrogen, the two atoms composing the molecule of

[1] For references see Smyth, Phys. Rev. **25**, 452 (1925); Hogness and Lunn, Phys. Rev. **30**, 26 (1927); Barton and Bartlett, Phys. Rev. **31**, 822 (1928).

[2] J. Franck, Trans. Faraday Soc. **21**, 536 (1925).

[3] Hogness and Lunn, Phys. Rev. **26**, 786 (1925).

carbon monoxide are different, providing the added interest that the CO^+ ion may dissociate to give either or both of the ions O^+ and C^+. Contrary to expectations, we have found that the ionization processes of carbon monoxide are not like those of nitrogen.

To follow the argument, it will be necessary that the reader have some idea of the apparatus and the experimental conditions. In the accompanying figure, we give, therefore, as we have previously done, a schematic picture of the arrangement of the electric and magnetic fields. Electrons from the filament F ionize molecules in the chamber J. These ions, under the influence of the fields V_2 and V_3 then take the path indicated by the arrows and in the chamber H are bent in a semicircle by a transverse magnetic field. The pressure in J is ten or fifteen times that in H. By varying the pressure in J, the free path of the ions may be varied accordingly. In resolving any group of ions into its constituent components, V_1 is kept constant at some convenient value greater than the ionization potential, V_2, and the magnetic fields are also kept constant, and as V_3 is varied, the electrometer deflections due to the ion current reaching the plate P are noted. The electrometer deflections are plotted against V_3 and sharp distinct peaks are obtained (see Fig. 3). From the V_3 value for these peaks, the e/m ratio for the ions can be calculated by the usual formula $e/m = 2V/H^2r^2$. Here r is the radius of curvature of the ions in the magnetic chamber and in this work was 7 cm. $V = V_3 + V_x$ where V_x is a portion of V_2, depending upon the position in the chamber J at which the ions are formed. When V_2 is small, $V = V_3$ approximately. H represents the magnetic field strength. The e/m ratio can also be determined by keeping V constant and varying the magnetic field strength. Where constant electrical conditions were desired, this was done. The ionization potentials are determined by decreasing V_1 until no ions are obtained. The apparatus was the same as that used by the present authors in a previously reported work on iodine.[4]

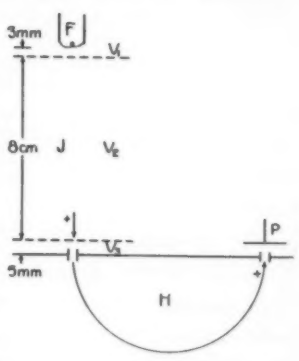

Fig. 1. Schematic arrangement of the fields.

The carbon monoxide was formed by dropping concentrated formic acid on concentrated sulfuric acid and was purified by potassium hydroxide and by a liquid air trap.

Carbon monoxide at higher pressures and lower temperatures will react to form CO_2 and free carbon, but at the temperature of the filament and at the pressures here employed, negligible quantities of CO_2, at most, could be formed even under equilibrium conditions.

The following processes have been found to occur:

$$CO = CO^+ + E^- \quad (1)$$

$$CO = O^+ + C + E^- \quad (2)$$

$$CO = C^+ + O + E^- \quad (3)$$

$$CO^+ + CO = C^+ + CO_2 \quad (4)$$

[4] T. R. Hogness and R. W. Harkness, Phys. Rev. **32**, 784 (1928).

Process (1) was found to occur at 13.9 volts (corrected) which checks the commonly accepted value of 14.2 volts[5] within the limits of accuracy of the present experiment.

Process (2) is the most doubtful of the processes found to occur. O^+ ion was always present in limited quantities and the ratio of the relative intensity of this ion to that of the CO^+ was found to be quite independent of pressure change. This much established that the O^+ ion was formed by the primary act of ionization. Upon lowering the velocity of the impact electrons, V_1, O^+ was found to be present in small quantities at potentials of V_1 so low that it could not, under these conditions, have been formed from CO. Using the spectroscopically determined value of 11.2 volts[6] for the heat of dissociation of CO and 13.6 as the ionization potential of the oxygen atom, we calculate 24.8 volts as the minimum potential at which O^+ could be produced by such a process. O^+ was, however, found somewhat below 20 volts. This O^+ produced below 24.8 volts resulted then from the presence of some impurity. It is practically impossible to rid the apparatus of the last traces of water vapor. Three months' continuous pumping reduced it to a quantity that would be entirely negligible if O^+ were not produced as a result of the ionization of the H_2O molecule. Barton and Bartlett[7] in describing an analysis of the ionization processes of H_2O, state that H_2O^+ and OH^+ were the principal ions formed and infer in the conclusion of their article that O^+ was not observed. If O^+ does not result from the ionization of H_2O, we are at a loss to account for its origin at the low potentials of V_1. The O^+ was not formed from oxygen as an impurity. We should then have observed O_2^+ with an intensity about five times that of the O^+ ion.[8] No trace of O_2^+ ion was observed. If, however, the intensity of the O^+ ion were plotted against V_1, the voltage applied to the impact electrons, it was found that this intensity dropped to a very small value at about 25 volts and then decreased at a much slower rate as the potential V_1 was lowered. If the portion of curve above 25 volts were extrapolated to zero intensity, a disappearing potential of about 24 volts (corrected) was obtained. We thus have reason to believe that the O^+ produced was due principally to the reaction of process (2).

Process (4), not being expected, was discovered accidentally. When V_2 was made 80 volts instead of the usual value of about 5 volts and when V_1 was decreased below 25 volts, there occurred a shift in the position of the peak of the intensity-V_3 curve. In Fig. 2, this phenomenon is shown graphically. When V_1 had a value of 30 volts, the intensity had a maximum at a value of 1700 volts for V_3, but when V_1 had a value of 21 volts, this peak occurred at about 1740 volts. To explain this, we must refer to Fig. 1. The field V_2 is of opposite sign to that of V_1 and electrons from the filament upon

[5] Birge, Nature **117**, 229 (1926). See also Compton and Mohler, Bull. Nat. Res. Council No. **48**.

[6] Birge and Sponer, Phys. Rev. **28**, 259 (1926).

[7] Barton and Bartlett, Phys. Rev. **31**, 822 (1928).

[8] See Hogness and Lunn, Phys. Rev. **26**, 723 (1926).

entering the region J, after passing through the first gauze, are retarded by the field V_2 such that only those in the upper portion of this region J have sufficient energy to ionize the gas molecules. The ions thus formed in this upper region then fall through almost all of the field V_2 and already having energy equal to almost the whole of V_2, a smaller value of V_3 is necessary to focus them on the collecting plate P than that which would be necessary if these ions had not acquired any energy from the field V_2. This condition is met with in the curve $V_1 = 30$ in Fig. 2. If, however, C^+ ions are formed as a result of a collision of CO^+ and CO this process will occur at some lower position in J and the C^+ ions thus formed will fall through a smaller portion of V_2 than in the former case, and, not having acquired as high a velocity as those previously considered, a larger value of V_3 must be employed to focus these ions on the plate P. The peak $V_3 = 1700$ volts is due to C^+ ions formed by process (3), and those at the peak $V_3 = 1740$ by process (4). Using 11.2 volts[6] as the heat of dissociation of CO and 11.3 volts[9] as the ionization of the carbon atom, we calculate 22.5 as the minimum potential at which process (3) could occur. This is in agreement with the results given in Fig. 2. At 21 volts, the peak due to this process has disappeared. Energetically, process (4) can occur and the peak at 1740 volts, due to process (4) should persist until V_1 was reduced to about 14 volts (corrected). This was also found to be the case. Furthermore, if our explanation is correct, the ratio of the intensity of the peak due to process (4) to that due to process (3) should increase with pressure and the ratio of the intensity of the CO^+ ion peak and that due to process (4) should also vary with pressure. Table I shows that these expectations were completely fulfilled. The ionization potential for process (2) was found to be 22.8 volts. Each of the several values used in obtaining this average deviated from it by less than 0.5 volt.

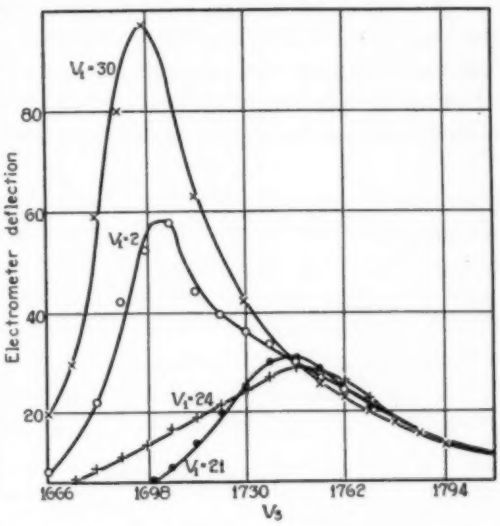

Fig. 2. The peaks for C^+ ions obtained with various values of V_1

Combining this value with the ionization potential of the carbon atom, we obtain 11.5 volts or 265,000 calories as the heat of dissociation of CO. This is about 7000 calories greater than that obtained from band spectra data.[6] All ionization potential determinations were corrected by using argon with an ionization potential of 15.4 volts as the calibrating gas.

[9] Millikan and Bowen, Proc. Nat. Acad. Sci. **13**, 531 (1927).

No such shift of the intensity peak as that observed with C^+ was found for the O^+ ion but from the position of the O^+ peak when V_2 was made large, we conclude that the O^+ ion is formed at the top of the chamber J, indicating that its formation from CO is a primary process. This substantiates our previous conclusions regarding the formation of this ion.

TABLE I.

Pressure $\times(10)^6$:	8	20	230	410
Intensity of CO^+ for $V_1=21$ volts / Intensity of C^+ for $V_1=21$ volts	440	385	74	25
Intensity of C^+ from process (3) for $V_1=28.5$ volts / Intensity of C^+ from process (4) for $V_1=21$ volts	9.5	5.5	1.6	0.7

Fig. 3 is presented to show graphically the relative intensities of the various ions and the resolving power of the apparatus. Here the m/e values are plotted against the positive ion current, in arbitrary units, reaching the

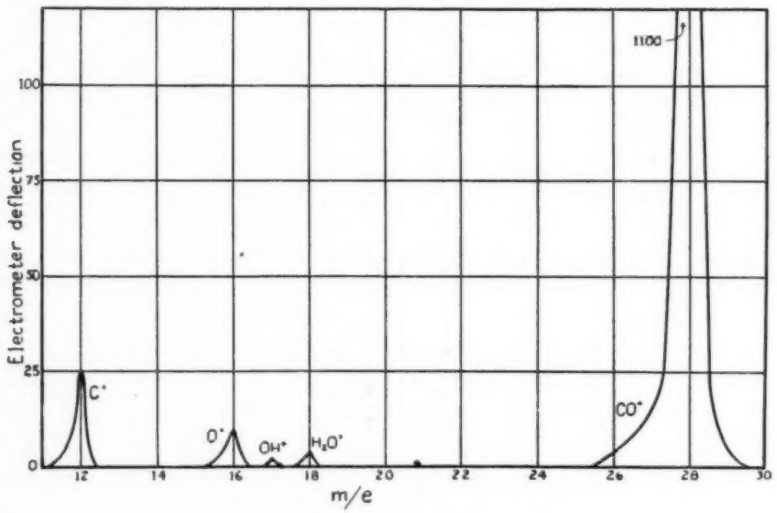

Fig. 3. Relative intensities of the various ions.

collecting plate P. It will be noted that the intensities of the O^+ and C^+ are relatively much smaller than that of CO^+. By either varying the sensitivity of the electrometer or the electron current, it was easily possible to get large electrometer deflections of these ions.

At the higher pressures employed a trace of a peak corresponding to the ion CO_2^+ could be detected and the intensity of this peak increased somewhat as the pressure was increased but at no time was the intensity of this ion greater than 0.2 percent that of the CO^+ peak. It is possible that such corre-

spondingly small amounts of CO_2 could be formed by the reaction $2CO = C + CO_2$ at the filament. For this reason and because of its small intensity no conclusions regarding its origin can be made. An extremely small peak which might have been $(CO)_2^+$ was also observed. Using values of V_1 as high as 80 volts, we were unable to detect the presence of any doubly charged ions, nor were any negative ions found.

From the results of this investigation, we have shown that there are three principal ionization processes which may occur in a primary manner when the CO molecule is ionized by electron impact. As we have already pointed out, this is contrary to expectation since the similar N_2 molecule reacts in quite another way. CO^+ molecules in the excited states corresponding to the $X'A'$ and B' levels [5,6] do not have moments of inertia markedly greater than that of the normal CO molecule. Therefore, we should expect that when the CO molecule is ionized, it would not dissociate spontaneously, behaving like N_2 in this respect. By far the greatest proportion of the ionized CO molecules behave in this way. The fact that simultaneous dissociation into C^+ or O^+ does take place to a small extent very probably means that levels, other than those already known, with much larger moments of inertia of the CO^+ molecule do exist and that the probability of electron transition to these levels is small.

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UNIVERSITY OF CALIFORNIA,
JULY 25, 1928.

THE IONIZATION PROCESSES IN METHANE INTERPRETED BY THE MASS SPECTROGRAPH

By T. R. Hogness and H. M. Kvalnes

Abstract

The ionization processes occurring when CH_4 molecules are ionized by controlled electron impact have been determined with the aid of the mass spectrograph. CH_4^+ and CH_3^+ are the only ions formed, and by a study of their relative intensities under different conditions of pressure and voltage, it was found that both these ions are formed directly by the electron impact. The ionization processes are: $CH_4 = CH_4^+ + E^-$ (14.5 volts); $CH_4 = CH_3^+ + H + E^-$ (15.5 volts).

Isotopes of neon.—It has been definitely determined that besides the two isotopes of neon, Ne_{20} and Ne_{22}, there exists a third isotope with a mass of 21.

THE work here described was undertaken with the hope of obtaining the bonding energy between the CH_3 radical and the hydrogen atom in methane. The dissociation or bonding energy of diatomic molecules can be obtained from the data of positive ray analysis[1] and by applying the same methods to polyatomic molecules, it should be possible to determine the bonding energies of these molecules as well. If H^+ were produced directly from CH_4 by electron impact and if the minimum potential applied to the impact electron to produce H^+ from methane were known, the bonding energy could be determined by simply subtracting the ionization potential of the hydrogen atom (13.5 volts) from this minimum potential.

Unfortunately the H^+ ion is not produced by electron impact with CH_4 and, because of this, the principal object of the work has not been attained, but the processes that do occur when methane is ionized by impact electrons have been successfully interpreted.

The apparatus, with the exception of a few changes in minor details, and the method of analysis were the same as those employed by Hogness and Lunn.[2]

In the first experiments, tungsten filaments were used and under these conditions the ions CH_4^+, CH_3^+, CH_2^+, CH^+, C^+, H_2^+, and H^+ were found to be present. The intensity of the ions CH_2^+, CH^+, C^+, H_2^+ and H^+ were, under all conditions, very small and it was suspected that these ions were produced by ionization of the products of thermal dissociation of the methane by the filament. The tungsten filament was then replaced by a nickel-platinum oxide-coated filament which, at a much lower temperature, gave the same electron emission as that of the tungsten filament. With this new filament, only the ions CH_4^+ and CH_3^+ were obtained. Under no conditions was it now possible to get any evidence whatsoever of the H^+ ion.

To determine whether the CH_3^+ resulted from spontaneous dissociation accompanying the ionization of the CH_4 molecule or whether a collision of

[1] For references, see Hogness and Harkness, Phys. Rev. **32**, 784 (1928).

[2] Hogness and Lunn, Phys. Rev. **26**, 44 (1925).

the CH_4^+ ion with a neutral CH_4 molecule was necessary for the production of the CH_3^+ ion, the usual method of studying the relative intensities of these two ions as a function of the pressure in the ionization chamber was employed. In twenty-three determinations with the pressure varying all the way from 3×10^{-5} to 380×10^{-5} mm, the ratio of CH_3^+ to CH_4^+ was 1 ± 0.1 and since no variation of this ratio with pressure was found, it must be concluded that the CH_3^+ ion is produced directly upon ionization of the CH_4 molecule by electron impact. The two processes which occur may be represented by the following equations:

$$CH_4 = CH_4^+ + E^- \quad (1)$$

$$CH_4 = CH_3^+ + H + E^- \quad (2)$$

When an electron of sufficient energy ionizes a CH_4 molecule, it may do so in one of two ways; it may produce the stable CH_4^+ ion, or an unstable CH_4^+ ion which dissociates spontaneously into a stable CH_3^+ ion and a neutral

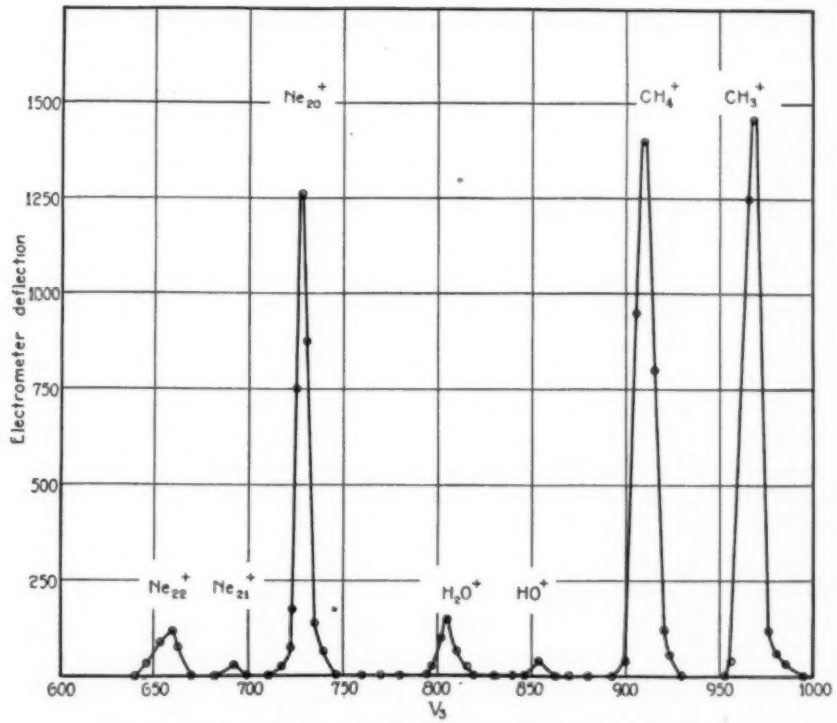

Fig. 1. Mass spectrograph curves for CH_4 together wih the curves for neon used for calibration.

hydrogen atom, but any CH_4^+ ion produced by electron impact cannot dissociate into a CH_3 radical and an H^+ ion. Furthermore, the probabilities for the occurrence of processes (1) and (2) are about equal. This constant ratio between the CH_4^+ and CH_3^+ ions was also maintained in mixtures of neon and methane. If any of the CH_4^+ or CH_3^+ ions were produced by impact of

the CH_4 molecule with the Ne^+ ion, the probabilities of the formation of either of these ions was also the same under these conditions. The accompanying figure shows this fact graphically and also shows the resolution which was obtained with the instrument. In this figure, the ordinates represent electrometer deflections and the abscissas the analyzing voltage applied to the positive ions. The m/e values from which the various ions were identified were calculated from $e/m = 2V_3/H^2r^2$ where H is the magnetic field strength and r the radius of curvature (5 cm), of the path of the positive ions in the magnetic field.

The ionization potentials of each of the two processes was determined by the usual method of lowering the voltage applied to the impact electrons until the peak of the particular ion just disappeared. To correct for initial velocities, contact potentials and instrument sensitivity neon was used as the calibrating gas. The ionization potential of neon was taken to be 21.5 volts[3] and referred to this the ionization potentials obtained in four different determinations are given in Table I. The value, 14.5 volts, of the second column represents the energy change in process (1) and that of the third column, 15.5 volts, that of process (2).

TABLE I. *Ionization potentials for CH_4^+ and CH_3^+.*

Expt. No.	CH_4^+	CH_3^+
1	14.45 volts	15.50 volts
2	14.50	15.50
3	14.50	15.50
4	14.50	15.83
Average	14.5	15.5

Mayer[4] obtained a value of 13.5 volts for the ionization potential of methane, Hughes and Dixon[5] 9.4 to 9.6 volts, and Hughes and Klein[6] 13.9 volts, Glockler[7] was unable to obtain a sharp break in the current potential curves obtained with methane and believed that but one process was taking place which had an ionization potential between 14.4 and 15.2 volts. Pietsch and Wilcke[8] obtained two distinct values of the ionization potential of methane, one at 14.58 ± 0.05 volts and one at 15.40 ± 0.05 volts. The first of these they interpreted correctly to be that of our process (1). The second value, however, they ascribed to the complete dissociation of CH_4 into gaseous atoms without ionization. The correct interpretation of this second value is that of process (2).

[3] Hertz and Kloppers, Zeits. f. Physik **31**, 463 (1925).
[4] Franz Mayer, Ann. d. Physik **45**, 1 (1914).
[5] Hughes and Dixon, Phys. Rev. **10**, 495 (1917).
[6] Hughes and Klein, Phys. Rev. **23**, 455 (1924).
[7] Glockler, J. Am. Chem. Soc. **48**, 2021 (1926).
[8] Pietsch and Wilcke, Zeits. f. Physik **43**, 342 (1927).

No negative ions, doubly charged positive ions or positive ion clusters were found.

Isotopes of Neon

The calibrating gas, neon, gave the positive ions, Ne_{20}^+ and Ne_{22}^+ in the ratio of ten to one as found by Aston[9] and by Barton and Bartlett.[10] There was, in addition to these ions, a small peak for Ne_{21}^+, which was always found when neon was in the apparatus (see Fig. 1) but was never obtained in the absence of neon. When pure neon was run at such conditions as to give greatest intensity of the Ne_{20}^+ ion, it was found that the intensity of the Ne_{21}^+ ion corresponded to about 2 percent of the sum of the intensities of the three ions of neon. In early work by Aston,[11] reference was made to finding a line in neon corresponding to Ne_{21}^+, and from its intensity he estimated its concentration in neon as being less than one percent by volume. In a later work by Aston,[9] no line for Ne_{21}^+ was found, but since poor results are claimed for Ne_{22}^+, it may be that the increased resolution of the apparatus which was used cut down the sensitivity for Ne_{21}^+ to such an extent that it could not be detected. Such effects are very pronounced in the apparatus used in the present work. The fact that Aston only finds H_2O^+ during the first few days after pumping out the apparatus likewise indicates that the absence of Ne_{21}^+ is a matter of intensity since H_2O^+ is always present in the type of apparatus used here.

The plot of the curve for the ions of neon published by Barton and Bartlett shows that the peak for Ne_{22}^+ starts at 20.7 so that any Ne_{21}^+ present would not be resolved.

If the peak for mass twenty-one were due to a hydride of Ne_{20}, then there should be a peak for mass twenty-three corresponding to the hydride of Ne_{22}. The calculated intensity for this peak is 1.6 scale divisions under the conditions referred to before, which is detectable when a specific search is made for such an intensity. No such peak was found, however. There are then three isotopes of neon of masses, twenty, twenty-one and twenty-two, respectively.

We wish to take this opportunity to express our indebtedness to Dr. M. J. Kelly of the Bell Telephone Laboratories for supplying us with the oxide coated filament, without which this work would have been much more difficult.

Chemical Laboratories,
University of California,
August 13, 1928.

[9] F. W. Aston, Proc. Royal Soc., **115A**, 487 (1927).
[10] Barton and Bartlett, Phys. Rev. **31**, 822 (1928).
[11] F. W. Aston, Phil. Mag. **39**, 449 (1920).

IONIC OSCILLATIONS IN THE GLOW DISCHARGE

By L. A. Pardue and J. S. Webb

Abstract

In an effort to correlate Whiddington's work on moving striae and Appleton's work on ionic osciallations from a striated discharge, it was found that the ionic oscillation phenomenon was sufficiently involved to warrant a detailed study. The discharge tube was of the hot cathode type, 3 cm in diameter and 26 cm long. The oscillations were detected in three ways: first, by means of curved plates on the tube which were connected in parallel with the tuning condenser of the receiver; second, by direct inductive "pick-up" from the tube itself; third, by inductive "pick-up" from a coil in series with the tube. By these methods frequencies from 15×10^4 to a few hundred cycles were obtained, the higher frequencies being detected on an auto-dyne receiver, the lower frequencies on a straight low-frequency amplifier. Characteristic curves obtained show an increase of frequency with filament current, an increase of frequency with anode potential and a decrease with pressure except at the lower pressures where the frequency increases, passing through a maximum. With a varying pressure and without plates on the tube, oscillations do not occur when there are sharply defined striae but begin just as striae begin to diffuse, decreasing in frequency and becoming audible when a uniform glow fills the tube.

Introduction

THE phenomena in the discharge tube have long been the study of many workers but still present many unsolved problems. The work of Whiddington[1] and of Appleton[2] has suggested possibilities that may lead to interesting and worthwhile conclusions. It occurred to the writers that a correlation between moving striae as observed by Whiddington and ionic oscillations from a striated discharge as observed by Appleton might be found. Before making this investigation it was found important to study the dependence of the oscillations upon pressure, voltage and filament-current variations. The object of this paper is to report the results of this work.

The Apparatus

The discharge tube was of the hot cathode type, 3 cm in diameter and 26 cm long. The oxide-coated filament was heated by a current which could be kept quite constant, the necessity for which will be evident when a characteristic curve showing the relation between frequency and filament current is studied. The effect of a changing pressure was observed by permitting the pressure of the air in the tube to increase very slowly by leakage into the vacuum system. The rate of leakage was less than 0.1 mm in three hours. The anode potential was varied by a potentiometer around a storage battery making available as much as 640 volts. The oscillations were detected in three ways: first, by means of curved plates on the tube which were connected in parallel with the tuning condenser of the receiver; second, by direct inductive "pick-up" from the tube by detector, having inductance of detector close to the tube; third, by inductive "pick-up" from an inductance in series with the tube, having this inductance and the detector far enough away from the tube to eliminate detection by the second method. In the first and second

[1] Whiddington, Engineering **120**, 20 (1925).

[2] Appleton, Phil. Mag. **45**, 879 (1923).

methods the inductance shown in series with the tube was not in the circuit. These arrangements will be evident when Fig. 1, giving a diagram of the apparatus, is inspected. The auto-dyne circuit used has the advantage of functioning as an oscillator and detector. Since the higher frequencies were far out of the range of audibility it was necessary to be able to detect a beat frequency. A separate oscillator and detector might have been used but the auto-dyne circuit is particularly advantageous in that it functions as both. The oscillating circuit was calibrated with a high-precision wave-meter. The vacuum system including pumps and McLeod gauge is not shown.

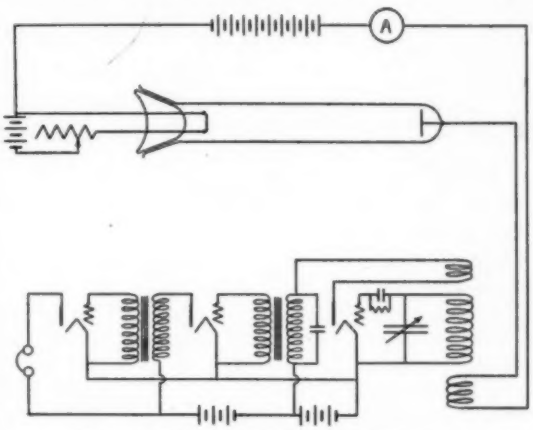

Fig. 1. Diagram of the apparatus.

Theoretical Considerations

It is a well established fact that a constant e.m.f. impressed upon a discharge tube causes a varying current to flow through the tube. This is doubtless due to a changing potential gradient within the tube caused by a shifting space-charge concentration. In the present work frequencies were observed from 15×10^4 down to a few hundred, the high frequencies being detected on the auto-dyne receiver and the lower frequencies on a straight low-frequency amplifier. These observations are not to be confused with periodic discharges from tubes which depend for their periodicity on resistance and capacity in parallel with the tube.[3] The constants of the circuit do not affect these ionic oscillations. The frequency depends on pressure, anode potential and filament current as the data will show.

The recent work of I. Langmuir, L. Tonks and H. Mott-Smith[4] in theory and in corroborating experiment indicates that if a "plasma" contains n electrons per unit volume (and an equal number of positive ions) and if the concentration of electrons be slightly altered, the concentration in trying to return to its original value may cause to occur waves (compressional waves) whose frequency is independent of the wave-length. The frequency is given by the equation

$$\nu = e(n/\pi m)^{1/2} \qquad (1)$$

This equation applies to electronic space-charge. Usually, however, in a gaseous discharge the electrons are at a very high temperature relative to the positive ions. It is assumed that the electrons tend to a uniform concentration while the positive-ion concentration will vary, setting up potentials given by the Boltzmann equation. The positive ions will oscillate with a frequency which will approach the value given by Equation (1) where m is the mass of the positive ion. This value will be reached when the temperature of the electrons becomes infinite.

[3] Penning, Phys. Zeits. **27**, 187 (1926).

[4] In a paper which will soon appear in the Proceedings of the National Academy of Sciences.

From Appleton's paper one is led to believe that oscillations occur in sharply defined striae but we do not find this to be the case. Our observations indicate that oscillations do not exist when the striae are sharply defined but begin at the instant diffusion between adjacent striae begins and continue until all forms of striations disappear and a uniform glow fills the tube. At this point the oscillations become unstable and finally subside as the pressure is increased. This unstable condition lasts over a fairly wide range of pressures starting at 0.07 to 0.1 mm. The beginning of instability depends upon the filament current and plate voltage. In the receiver this condition seems to consist of the original oscillations superimposed on a background of noises or "atmospherics."

Frequency Variations

The results obtained by the three methods previously mentioned were generally the same except for one difference to be pointed out which was found when plates are used on the tube. The production of the oscillations seemed to be confined within the tube and to be governed by the physial conditions there. A condenser shunted around the tube had no noticeable effect. The effect of pressure was found to be the most interesting. The relation between frequency and pressure is shown in Fig. 2. From Eq. (1) it is to be expected that

$$\nu \propto n^{1/2}$$

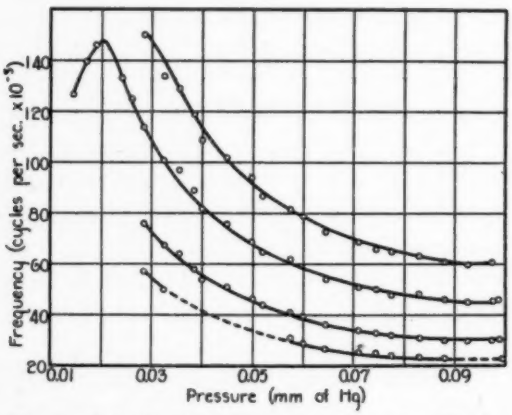

Fig. 2. Relation between frequency of oscillation and pressure.

Townsend[5] gives an equation for ionization by collision, $n \propto pe^{-cvp/x}$, in which c is the reciprocal of the electronic free-path at the pressure of 1 mm, p is the pressure in mm, x is the field strength and v the ionizing potential. It follows when p is varied, that the number of electrons, n, per cm^3, and correspondingly the frequency, rises to a maximum at $p=x/cv$, then falls. The curves in Fig. 2 are in accord with this. From the data chosen, which are typical of many trials, there are at least four frequencies at any given pressure. The values of the frequencies suggest the existence of two independent frequencies each having a harmonic. There was at times evidence of other frequencies and of harmonics higher than the first. In the observations, as shown in Fig. 2, one finds that the frequencies are almost exactly in the ratios of the integers 3, 4, 6, 8. These frequencies may well be the harmonics of an unobserved fundamental frequency. The point of maximum frequencies is displaced toward the lower pressures from the computed value. The computation is based on a uniform fall of potential throughout the tube. Since the fall is largely in the cathode region it follows that the average field strength in the region of the positive column is much lower.

[5] Townsend, Electricity in Gases—p. 294, Oxford, 1915.

On this basis the turning point is much more reasonable. The dotted portion in one of the curves shows a part in which the capacity range was not sufficient to accommodate all four frequencies. A large amount of other data of which Fig. 2 is typical shows that all the frequencies have a turning point at the same pressure. The anode potential was kept constant at 640 volts and the filament current at 6.3 amp.

In Fig. 3 the relation between frequency and anode potential is shown. The Townsend equation indicates that the frequency varies exponentially with the reciprocal of the anode potential. In Fig. 3 the pressure is 0.01 mm and the filament current 6.4 amp. Fig. 4 shows how variations in the filament

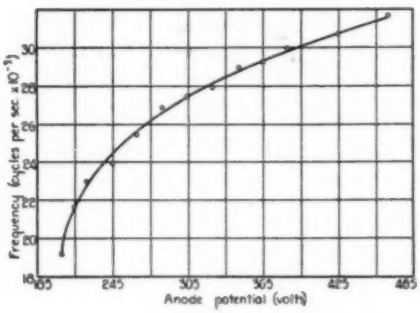

Fig. 3. Relation between frequency of oscillation and anode potential.

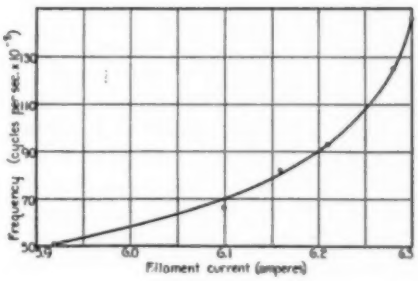

Fig. 4. Relation between frequency of oscillation and filament current.

current affect the frequency. The principle of electronic emission from hot bodies as expressed by Richardson's equation governs the number of ionizing electrons which in turn determines n in the equation, the other quantities remaining constant. It is then not surprising that the curve has the shape it does. The anode voltage in Fig. 4 is 640 volts and the gas pressure is 0.01 mm.

Conclusion

The foregoing results are being reported now as at the close of one stage of the work. The writers hope to be able to continue the work at some immediate future time, to investigate in particular one phase of the problem which may lead afield from the general course of this work. This has to do with attaching plates to the tube. When they are attached one finds a slightly different condition. At the lower filament temperatures, when the discharge fills the tube, the oscillations are audible and can be heard as mechanical vibrations of the tube under certain conditions. At the higher temperatures the oscillations become inaudible but can be detected as beats These occur even when striae are present. It is possible that the plates affect the potential gradient within the tube but this point has not been determined.

It is a pleasure to acknowledge the valuable suggestions and advice, tendered by Professor C. C. Bidwell of Lehigh University, throughout the course of this work; also the information given by Dr. Irving Langmuir of the General Electric Company, in advance of publication.

Physical Laboratory,
Lehigh University.
June 11, 1928.

CRITICAL PHOTOELECTRIC POTENTIAL OF CLEAN MERCURY AND THE INFLUENCE OF GASES AND OF THE CIRCULATION OF THE MERCURY UPON IT

By Wayne B. Hales

Abstract

The apparatus used by Kazda and Dunn for the determination of the critical photoelectric potential of mercury has been completely reconstructed. The stop-cocks, the grease of which was the source of contaminating vapors, have been replaced by mercury cut-offs and the high temperature cement used in the construction of the photo-electric cell has been replaced by a graduated quartz-Pyrex seal. Fresh clean mercury was returned to the still. With this new apparatus and under these new working conditions the long wave-length limit for running mercury has been found to be 2735A. The conditions within the apparatus have been found to be practically free from contaminating vapors so that the critical frequency has been found for stationary mercury, namely 2735 ± 10A, which is in entire agreement with Kazda for flowing mercury. This impurity in the old apparatus caused the photo-current to increase four-fold its original value in thirteen to twenty minutes after the still was turned off. It then slowly receded, falling below its initial value in three or four days. This increase in the photo-current was accompanied by a rise in the threshold to 2850A, thence falling in time to a constant value 2680A. In the apparatus as it now stands this same four-fold increase is not reached until some eighty hours after the still is turned off and remains perfectly constant indefinitely thereafter. The long wave-length limit for this maximum sensitivity was found to be 2910A.

Hydrogen, helium, argon, nitrogen, and water vapor in extremely small quantities in contact with the surface and also, except in the case of water vapor, dissolved in the body of the mercury, had no influence whatever upon the photoelectric behavior of the mercury or upon the rate of rise of sensitivity upon turning off the still except that each had a marked cleansing effect in reducing the concentration of the impurity which slowly contaminates the surface. Oxygen had a decided reducing effect upon the threshold value, bringing it down to 2555A in eighteen hours.

I. Introduction

THE phenomenon of photoelectric fatigue has for years been the subject of many exhaustive experimental studies. This fatigue has been explained in all cases as being due to either chemical, physical, or electrical modifications of the surface. In fact, Hallwachs, Wiedemann and others maintained that it is the modified surface and not the material itself that exhibits these photoelectric properties and if absolutely clean surfaces could be had they would be insensitive to the action of light. The Hallwachs theory states that photoelectrons are due to adsorbed and absorbed gases; that the adsorbed layers of gas on the surface hinder the discharge of photoelectrons, while the absorbed gas in the metal assists the process of discharge of electrons. Without going farther into the discussion of these theories, it is now generally conceded through the work of Elster and Geitel, Pohl and Pringsheim, Millikan, and others that the photoelectric activity of a pure metal is an intrinsic property of that metal, and that no fatigue would be observed with a clean metallic surface in a perfect vacuum.

The greatest difficulty, therefore, in this field has been to realize these conditions. Metallic surfaces have been brought to a maximum of purity by prolonged heating at high temperatures, the surface again modifying itself slowly as it is brought back to lower temperatures. In 1923 Kazda succeeded in obtaining the most satisfactorily clean surface ever hitherto had. His measurements were made on a flowing surface of mercury which very recently had condensed from the vapor state. This surface was in contact with the contaminating impurity for only a few seconds, a time altogether too short for the contamination to become effective. He was thus able to establish accurately the critical photo-electric potential for flowing mercury at 2735 ± 10A, and this as an intrinsic property of mercury itself. The fact that his work was done at ordinary room temperature was a distinct contribution to this field of investigation. Kazda found, however, that as soon as the mercury surface became stationary it was immediately changed either by gases[1] modifying its surface or else through some molecular arrangement which was different when stationary from that when flowing. Kazda, therefore, was never quite sure but that his value of 2735A for the critical potential of mercury was characteristic only of a moving mercury surface.

In 1924 Dunn[2] began an investigation with the same apparatus to determine the cause and nature of the surface contamination. He found by using a radioactive leak that the photo-current was increased four times its initial value when the mercury surface became stationary and then slowly receded below its initial value. The threshold immediately changed from 2735A to 2850A thence falling in three or four days to 2680A. Stopcocks were used in Kazda's apparatus. Among other things Dunn investigated the effect of the vapor from stop-cock grease upon the photoelectric behavior of mercury by inserting a small quantity in a lateral tube. He found that when liquid air was taken off this tube the impurity was present in the apparatus in sufficient quantity to attack the running surface regardless of how fast the surface was changing, giving this same threshold value of 2850A.

According to this then it is possible for the flowing surface to be modified. The thought, therefore, presented itself that the high temperature cement which was used in the construction of the photo-cell and which was immediately above the mercury, together with the vapors arising from the stop cock grease, could also attack the running surface and that 2735A is the threshold value for the contaminated surface.

Furthermore, the recent work of Sophie Taubes,[3] wherein she established 3043 ± 20A as the critical photoelectric potential of mercury drops suspended in a Millikan condenser, makes it desirable again to determine the threshold wave-length by Kazda's method after every possible source of contamination has been removed. To determine the effect of these changes in the apparatus on the photo-electric behavior of mercury and to investigate the modifica-

[1] Kazda, Phys. Rev. **26**, 643 (1925).

[2] Dunn, Phys. Rev. **29**, 693 (1927).

[3] Sophie Taubes, Ann. d. Physik **76**, 6, 629 (1925).

tions introduced when various gases were present in the apparatus, the present study was undertaken.

II. Apparatus

The mercury still, Faraday cage arrangement, the quartz mercury arc, the source of ultra-violet light, the Hilger monochromator, and Dolezalek electrometer for measuring photo-current were essentially the same as described in Kazda's and in Dunn's papers. On the other hand all the glass parts of the apparatus were newly constructed and carefully cleaned and the photoelectric cell completely remodeled. The iron cup, which held the mercury in the photo-cell, was held firmly in place in the old apparatus by means of a high temperature cement. This cement which could be the source of contaminating vapors was eliminated in the new apparatus, the cup being mounted on a cone of invar so shaped as to fit in the ground glass joint. A stiff spring passed from its lower end through the glass and held the cup firmly in place.

The quartz window above the Faraday cage was originally sealed to the photoelectric cell by means of high temperature cement. This was replaced by a quartz-Pyrex graduated seal. All stop-cocks were replaced by mercury cut-offs, thus eliminating practically every source of contaminating vapors. Both still and photoelectric cell were connected through liquid-air traps to two stages of condensation pumps, these being supported by a Cenco Hyvac pump. Fresh mercury, after being cleaned by filtration, washing, and distillation, was returned to the still and cell.

The relative intensities of the lines from the mercury arc were measured by means of a delicate vacuum thermopile consisting of a single couple connected to a high sensitivity galvanometer. The photo-sensitivity and threshold values were measured and plotted as described in the papers of Kazda and Dunn.

III. Diffusion of Hydrogen Through Mercury

Much time was spent in the study of the diffusion of hydrogen through the mercury and observing the effects produced upon the photoelectric behavior of mercury. This was done with the old arrangement of the apparatus which was admirably adapted for such a study. Dunn found that hydrogen present in small quantities in the cell had no observable effect upon either the threshold of the flowing mercury or the rate of rise of sensitivity upon turning off the still and allowing the surface to become stationary. However, when hydrogen was admitted only into the still and the mercury was allowed to condense for two hours in an atmosphere of hydrogen, striking evidence was furnished that hydrogen had entered into solution with the mercury and passed over into the cell where it modified the action of the contaminating impurity upon the surface of mercury. This was revealed in the fact that the maximum sensitivity of the surface was reached in 120 minutes after the still was turned off, whereas without hydrogen present this surface condition was reached in fifteen minutes. The rate at which the sen-

sitivity receded was much less with hydrogen present than without. The maximum threshold of 2850A was found to be the same in both cases.

Dunn's experiments on hydrogen were further extended by observing whether hydrogen could diffuse from the still through the mercury to the cell when the still was not running. Another run was made in which the hydrogen was not admitted into the still until 22 minutes after the still was turned off and the mercury became perfectly quiet. The results are plotted in *C* of Fig. 1, curve *B* being the normal effect in vacuum.

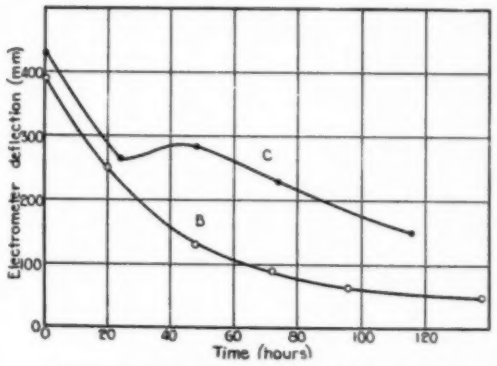

Fig. 1. Change of photo-sensitivity with time: *B*, normal effect in vacuum; *C*, showing effect produced by H_2 diffusing through 30 cm of mercury.

It will be noticed that for the first 24 hours the curves are identical. During the next 24 hours the hydrogen has succeeded in diffusing through the mercury and has changed the photoelectric sensitivity. The corresponding effect upon the threshold was observed.

These experiments were repeated and showed identically the same effect. They furnish very striking evidence that hydrogen will diffuse through such a small tube filled with mercury, the presence of it being detected by the change in the photoelectric behavior of the mercury. The column of mercury in this case was 30 cm long and 5 mm in diameter.

IV. Comparison of the Critical Potential for Flowing and Stationary Mercury

After the data discussed in section III were taken the whole apparatus was rebuilt as mentioned in section II.

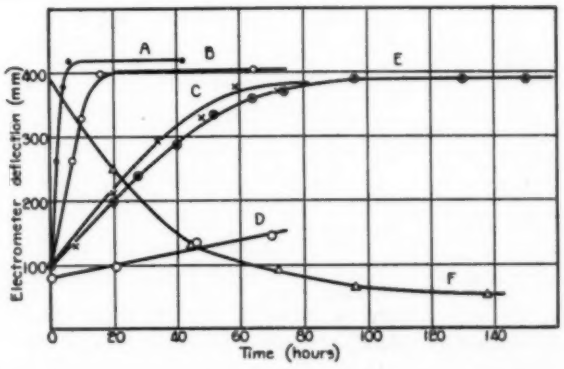

Fig. 2. Change of photo-sensitivity of stationary mercury: *A*, after four days of pumping; *B*, after eight days of pumping; *C*, after sixteen days of pumping; *D*, after two months pumping and washing; *E*, after prolonged pumping; *F*, characteristic curve given by old form of apparatus.

The results now obtained are given in Figs. 2, 3, 4, and 5. All curve showing the change of photoelectric sensitivity with the time were taken with the line λ2653A. After the mercury was placed in the still the pumps and still were operated during the day-time for four days before a reading was taken. The first set of readings is plotted in Fig. 2A. The photo-current is seen to increase four times its initial value in 6 hours and then remain constant for the next 34 hours. Curve *B* shows the change after four more days of pumping during which time the still was run intermittently for periods of 2 to 4 hours. Curve *C* is the same after 16 days pumping and reveals the same four-fold increase in photo-current in 60 hours, remaining constant thereafter. Curve *D* shows the rate of rise after pumping for two months during which time the apparatus was washed several times by helium, argon and hydrogen, these gases being introduced into the apparatus for the purpose of a study to be discussed in section V. *It will be noted in D that the apparatus is so free from contaminating vapors that the surface remains practically constant for 24 hours after the mercury surface becomes stationary.*

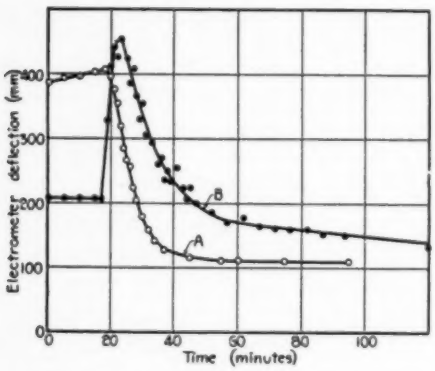

Fig. 3. Change of photo-sensitivity upon breaking up a surface held stationary for four days. *A*, new form of apparatus; *B*, old form of apparatus.

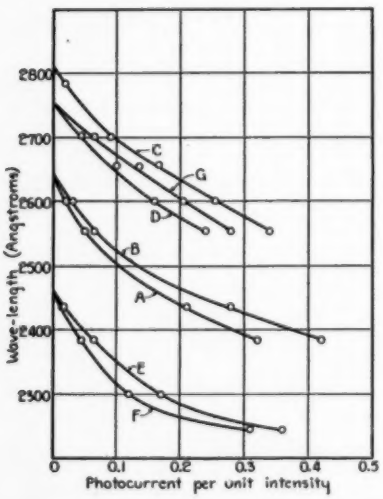

Fig. 4. Change of threshold of mercury. *A* and *B*, for flowing mercury, $\lambda_0 = 2735$A; *C*, maximum threshold after little pumping, $\lambda_0 = 2910$A; *D* and *G*, maximum threshold after prolonged pumping, $\lambda_0 = 2850$A; *E* and *F*, for stationary mercury in contact with dry air at atmospheric pressure for 30 min. and over night, $\lambda_0 = 2755$A

During the course of this experiment a leak developed and it became necessary again to change the mercury in the still. After prolonged pumping the data plotted in Fig. 2E were taken and observed for 398 hours. *During all the time after it had reached a steady value the electrometer deflection did not vary more than ±20 mm from 390 mm.* Curve *F* of Fig. 2 is a characteristic curve always obtained with the old apparatus and is given here for comparison purposes only.

Fig. 3B is a curve obtained from the old apparatus showing the changes produced in the photo-current when the mercury surface which had been stationary for three or four days was broken up by turning on the still. In twenty minutes the condensation of mercury in the still begins to break up the con-

taminated surface. The photo-current immediately rises to a maximum value and in about three hours returns to its normal value. During its return to normal the photo-current fluctuates by as much as 25 mm. This is shown by the scattered nature of the points through which curve *B* of Fig. 3 is drawn.

Curve *A* of Fig. 3, is the same phenomenon observed with the reconstructed apparatus. It will be noticed that these fluctuations are entirely absent, that all the points lie on the curve, and that the photo-current reaches its normal value in one hour after the still is turned on as compared with three hours for the old apparatus. This is added evidence that the contaminating vapors are present in very much less quantity than formerly.

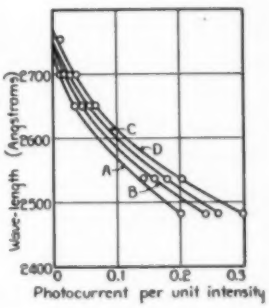

Fig. 5. Change of threshold of mercury in vacuum. *A*, flowing surface, $\lambda_0 = 2732$A; *B*, surface stationary 21 hours, $\lambda_0 = 2743$A; *C*, surface stationary 46 hours, $\lambda_0 = 2755$A; *D*, surface stationary 70 hours, $\lambda_0 = 2770$A.

Fig. 4 contains some threshold curves made with the new apparatus. Curves *A* and *B* represent runs made on flowing mercury locating the critical photoelectric potential at 2735 ± 10A, exactly the same as found by Kazda and Dunn. Curve *C* was taken at the time of maximum sensitivity during the early stages of pumping. This gave a threshold of 2910A. This was always a reproducible value when air was admitted to the apparatus two or three times in immediate succession. Since this maximum sensitivity was maintained for so short a time in the old apparatus Dunn was never able to make a successful determination of the maximum threshold in the usual way. His constant value of 2850A could reasonably have been 2910A. In fact, this 2910A value was observed by Kazda in his measurements with hydrogen in the cell. However, in the apparatus as it now stands after prolonged pumping the threshold for maximum sensitivity becomes constant at 2850A as shown by curves *D* and *G*. Curve *E* was obtained when the clean mercury surface had been exposed to dry air at atmospheric pressure for thirty minutes. This air was admitted through four long drying tubes containing $CaCl_2$ and P_2O_5. Curve *F* is the same as for *E* except that the air was left in contact with the mercury over night. The long wave-length limit for a mercury surface thus modified by dry air is quite definitely placed at 2555A units. This fact will be referred to in section V. The curves in Fig. 5 were taken at the same time as the data for curve *D*, Fig. 2. Curve *A*, Fig. 5, gives the threshold of 2732A for the flowing surface. Curve *B* gives the value 2743A for the surface which has been stationary for 21 hours. Curve *C* gives the value 2755A for the surface standing 46 hours and curve *D* gives the value 2770A for the surface standing in vacuum 70 hours. A threshold run taken 10 hours after the surface became stationary did not show any change in this critical frequency. These curves were taken after two months of pumping and washing with inert gases. They reveal, together with Fig. 2D that the apparatus is practically free from contaminating vapors, thus

affording an excellent opportunity to study the effect of different gases in modifying the photoelectric behavior and in changing this critical photoelectric potential.

Discussion of results. These data taken in high vacuum permit the following conclusions to be drawn:

First. The critical photoelectric potential for flowing mercury has been found to be the same in the new and old apparatus. This means that the impurities in the old apparatus were not present in sufficient quantities to change its threshold value. This also more firmly fixes 2735A as the long wave-length limit for clean mercury since it was done with new mercury and under new working conditions and constitutes an independent check of Kazda's work.

Second. The impurity was present in sufficient concentration in the old apparatus to make it uncertain whether the threshold of 2735A was unique to a turbulent flowing surface and whether the same threshold would obtain for an absolute quiet surface. Threshold values determined two hours and, later, ten hours after the surface became stationary, showed no change whatever in the critical frequency. It can be stated with certainty, therefore, that the *critical photoelectric potential for moving mercury is identical with that for stationary mercury and that this value is* $2735 \pm 10A$.

Third. The impurity in the old apparatus which caused the rapid rise of photo-current to four times its initial value in 20 minutes is now greatly reduced in concentration as this same four-fold increase in sensitivity is not reached until about 80 hours after the still is turned off. This maximum value has been observed to remain constant for 398 hours.

Fourth. Dunn did not know whether the following decrease in sensitivity was due to further increase in the deposit of but one impurity or whether it was due to the action of a second impurity which acted very much slower than the first. These experiments with the new apparatus clearly show that it must have been a second impurity, probably coming from the high temperature cement, which is entirely absent in the new apparatus. During six months of observation not a single instance was ever noted when this sensitivity ever decreased. One case was observed for 398 hours without any decrease occurring.

Fifth. Two theories are given to explain the increase in sensitivity. First: A layer of molecules of the impurity is slowly adsorbed on the surface of mercury, the presence of which facilitates the release of the photoelectrons from the surface, thus increasing its sensitivity. When a unimolecular layer completely covers the mercury surface it has lost its power to adsorb more and the photo-current remains constant and after prolonged pumping the surface settles to a long wave-length limit of 2850A. Second: When molecules of the impurity are adsorbed by the mercury, a surface of the impurity is gradually substituted for the mercury surface and what is then measured is the photoelectric behavior of the impurity and not that of the mercury.

V. Effect of Gases on this Stationary Critical Potential

The gases studied were hydrogen, helium, argon, water vapor, nitrogen, and oxygen. They were introduced into the apparatus in the above mentioned order. Each gas-generating apparatus could be attached without permitting air to enter either the cell or still compartments. The apparatus was always thoroughly pumped out, the pumps operating for three or four days, before successive gases were admitted.

Hydrogen. The hydrogen was generated electrolytically, the water vapor being taken out by circulating brine and P_2O_5. Traces of oxygen were eliminated by holding the gas in an atmosphere of sodium vapor at 110°C for three or four hours. The hydrogen, as well as all other gases except water vapor, was then passed through an activated charcoal trap colled to liquid-air temperature. The hydrogen, when in the cell or dissolved in the mercury in the still, did not change the photoelectric behavior of the mercury. Even when hydrogen of 3 cm pressure was in contact with the surface for 48 hours and then pumped off, no apparent changes from the normal effects were seen. Curves *A* and *B*, Fig. 6, show the effect of hydrogen when dissolved in the mercury, *A* being the normal effect, *B* the hydrogen effect. There is not sufficient difference to attribute any real effect to the hydrogen. Comparing this with similar curves obtained by Dunn we see a marked difference. The effect in curve *B*, Fig. 6, would be expected to be more normal since the impurity upon which hydrogen manifests itself is practically absent from the apparatus.

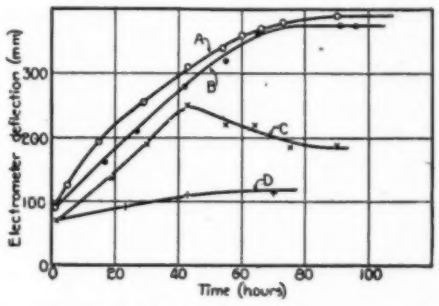

Fig. 6. Change of photo-sensitivity: *A*, normal effect in vacuum; *B*, effect of hydrogen dissolved in mercury; *C* and *D*, effect of water vapor released from 95 percent H_2SO_4 solution at −20°C and at 20°C.

Helium. Helium was taken from a drum of the Texas source and was purified by circulating it through a trap held at 500°C. The trap contained copper shav ings, which removed the oxygen, magnesium ribbon, which removed the nitrogen, and copper oxide, which removed the hydrogen. After passing over P_2O_5 and through activated charcoal at liquid-air temperature it was sufficiently pure for the purpose of the experiment. Observations taken when helium was present in the cell only and when dissolved in the mercury showed no change from normal behavior, either upon the surface sensitivity or upon the critical potential.

Argon. Argon taken from a flask furnished by the General Electric Company was introduced into the apparatus and showed the same lack of effect. No change was observed in the rate of rise of sensitivity or upon the critical

frequency because of the presence of these three gases, namely, hydrogen, helium, and argon. The only effects these three gases had was that of washing the impurity out of the apparatus and thus reducing the rate of rise of photoelectric sensitivity.

Water vapor. Water vapor was introduced into the apparatus early in the experiment by joining a lateral tube between the photo-cell and the liquid-air trap. The tube containing the water vapor was separated from the apparatus by a mercury cut-off so that vapor could be held and released at will. To reduce the concentration of water vapor five drops of distilled water were dissolved in ninety five drops of concentrated sulphuric acid. An approximation from available tables shows that the vapor pressure for such a mixture is not larger than 0.01 mm at ordinary temperature or 0.001 mm at −20C, the temperature of a salt and ice mixture. The effect of the water vapor on the photo-current is shown in curves *C* and *D*, Fig. 6.

For the first forty hours the sulphuric acid-water mixture was held at −20°C by means of a salt and ice mixture. The behavior during this time was quite normal. At this time the cooling mixture was taken off and the sensitivity thereafter fell. The threshold, however, remained constant at 2785A, and is shown in curve *B* of Fig. 7. Curve *D* of Fig. 6 was taken for water vapor freed from the solution at ordinary room temperature where the pressure of water could be from 0.01 to 0.05 mm. The rate of rise is seen to be very much slower. The threshold for this case after 20 hours was found to be 2800A, and remained constant for the next 50 hours. This is given in curve *C*, Fig. 7. It is safe to conclude, therefore, that 2800A is the critical potential characteristic of mercury in the presence of small quantities of water vapor. Kazda's statement that extremely small quantities of water vapor had a marked effect upon stationary mercury and raised its long wavelength limit, has not been checked in this experiment, but rather the conclusion is drawn that extremely small quantities of water vapor do not materially change the photoelectric behavior of mercury. Furthermore, this is concurrent with conclusions drawn by Richardson[4] for the action of water vapor upon a potassium surface.

Nitrogen. Nitrogen was prepared by removing the oxygen from the air by slowly sucking air through six wash bottles, the first four containing copper trimmings and equal amounts of concentrated ammonium hydroxide and concentrated ammonium chloride solution. The fourth bottle showed no coloration indicating that all the oxygen had been removed. The last two wash bottles contained concentrated solutions of sulphuric acid and removed all traces of water vapor.

At the time nitrogen was introduced the apparatus had been pumped out for two months and was practically free from contaminating vapors. The method used to determine the effect of nitrogen was to stop the still and observe the change in critical frequency after 24 hours; first, when the surface stood in vacuum and, second, when it had stood in 10 cm of nitrogen.

[4] Richardson, Proc. Roy. Soc. A107, 387 (1900).

The effect in both cases gave this critical frequency as 2750A. After the surface had stood for 91 hours in the presence of 10 cm pressure of nitrogen the long wave-length limit had risen to 2800A. This threshold determination is shown graphically in curve *D*, Fig. 7.

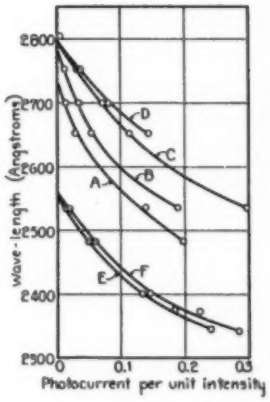

Fig. 7. Change of threshold of mercury. *A*, for flowing mercury; *B*, for stationary Hg 40 hours in presence of water vapor released at $-20°C$, $\lambda_0 = 2785A$; *C*, for stationary Hg 20 hrs. in presence of water vapor released at 20°C, $\lambda_0 = 2800A$; *D*, for stationary Hg 91 hrs. in presence of nitrogen at 10 cm pressure, $\lambda_0 = 2800A$; *E* and *F*, for stationary Hg 18 and 52 hrs. in presence of oxygen at 5 cm pressure, $\lambda_0 = 2555A$ and $\lambda_0 = 2560A$.

It is concluded that mercury is insensitive to the action of nitrogen in this molecular form.

Oxygen. The oxygen was prepared by heating potassium permanganate to 400°C. The oxygen liberated was passed through a plug of glass wool, thence over P_2O_5, and then through activated charcoal held at liquid air temperature. When quantities of oxygen of less than 0.005 mm pressure were added to the cell no effect was noted on the threshold for the running mercury surface. When the still was turned off and the surface became stationary, 5 cm of oxygen was admitted to the cell and still. After 18 hours this was pumped off and a threshold determination made. It is represented in curve *E*, Fig. 7, giving a threshold of 2555A. Five cm of oxygen was again placed in the still and cell without disturbing this surface. After another 52 hours the oxygen was pumped off and a threshold run made. This is represented in curve *F*, Fig. 7, giving a threshold value of 2560A. If these two curves are compared with curves *E* and *F* of Fig. 4, which resulted when dry air was in contact with the stationary mercury surface, we find exactly the same critical frequency appearing. We can conclude, therefore, that the only element in dry air which attacks the mercury surface is the oxygen and the critical frequency thus determined is for a mercury oxide film. This value was checked on a second determination similar to the above. The critical photoelectric potential for a mercury surface in contact with pure oxygen can be placed at $2555 \pm A$.

Stop-cock grease. While no special attempt was made to determine the effect of stop-cock grease upon the photoelectric behavior of mercury by introducing it specifically into the apparatus, it is evident that it plays a very important part. In fact the only way the rate of rise in sensitivity could be increased was by letting air into the apparatus through a stop-cock. This air would carry with it small quantities of grease vapor and thereby increase the concentration of the contaminating impurity.

VI. Summary

The results of this investigation may be summarized as follows:

First. Hydrogen will diffuse through a column of mercury 30 cm long and 5 mm in diameter from the still to the cell in a time between 24 and

48 hours and modify the action of contaminating vapors in the photoelectric cell.

Second. The changes in the construction of the photo-cell and apparatus have (a), eliminated entirely the impurity which attacked the stationary mercury surface and reduced its sensitivity; (b), practically eliminated the impurity which attacked the stationary mercury surface and increased its sensitivity; (c), resulted in conditions within the photo-cell so free from impurity that the surface remained practically constant for hours; (d), permitted the determination of the critical photoelectric potential for a clean stationary surface of mercury. Its value was found to be 2735 ± 10A, agreeing completely with the value found by Kazda for flowing mercury.

Third. Hydrogen, helium, argon, and nitrogen have no effect whatever upon the photoelectric behavior of either moving or stationary mercury. The surface is modified the same when in the presence of these gases as when in a high vacuum. Water vapor at very low pressure has no effect; at higher pressures it acts as an inhibiting agent to the action of other slight traces of impurity which attack the stationary mercury surface. Oxygen and dry air have a marked effect on the photoelectric properties and reduce the critical potential to 2555A in a short time.

In conclusion the author wishes to express his appreciation to Dr. Robert A. Millikan for setting him at work on this problem and for the helpful suggestions given during the progress of the experiment.

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CALIFORNIA INSTITUTE OF TECHNOLOGY
July 19, 1928

THE THERMIONIC EMISSION FROM CLEAN PLATINUM

By Lee A. DuBridge[1]

Abstract

The thermionic emission from thoroughly outgassed platinum in high vacuum has been measured to one-half percent over the temperature range 1360 to 1750°K, the temperatures being measured by careful optical pyrometry. The values obtained for the thermionic constants of the T^2 law are, when corrected for the Schottky effect, $b=72{,}820$°K, $\phi=6.27$ volts, $A=17{,}000$ amp/cm^2 deg^2. The value of ϕ is possibly in error by not more than 1 percent because of uncertainties in the temperature scale, and agrees within one-half percent with the value of the photoelectric work function previously obtained. The data confirm the previous announcement that for clean platinum A is 250 times greater than the theoretical value of 60.2 amp/cm^2 deg^2.

ALTHOUGH practically the first and for many years almost the only metal whose thermionic and photoelectric behavior was extensively studied, platinum has so completely failed to yield consistent results that the most careful existing measurements of the surface work function differ among themselves by as much as nearly 2 volts. It was early recognized through the work by Wilson,[2] Richardson,[3] Hallwachs[4] and many others that the cause of the discrepancies in both the photoelectric and thermionic work was to be found in the extraordinary tenacity with which the surface clung to slight traces of gas which greatly affected its electron emission. The work of many observers showed that as the surface was denuded of gases the work function steadily increased. In 1927 the writer[5] showed that by employing modern high vacuum technique and extending the time of outgassing of the metal to the order of one hundred hours a steady state could be reached in which both the photoelectric and thermionic work functions showed consistently a common value of approximately 6.3 volts. Pressure measurements indicated that this value was characteristic of a nearly gas-free surface. Clean platinum was thus established as the most electro-negative of any of the metals so far studied,—a fact not inconsistent with its position at the extreme right of the periodic table.

In addition, measurements of the constant A of the equation $I=AT^2e^{-b/T}$ yielded values 230 times greater than the theoretical value of 60.2 observed[6] for other metals. The possible significance of this result has been discussed elsewhere.[7] However in order to place the above values for the thermionic constants on a more exact quantitative basis it was necessary to extend the

[1] National Research Fellow.
[2] Wilson, Phil. Trans. **208A**, 251 (1908).
[3] Richardson, Emission of Electricity from Hot Bodies, Chap. IV.
[4] Wiedmann and Hallwachs, Verh. Deut. Phys. Ges. **16**, 107 (1914).
[5] DuBridge, Phys. Rev. **29**, 451 (1927); **31**, 236 (1928).
[6] Dushman, Phys. Rev. **21**, 623 (1923); **25**, 338 (1925).
[7] DuBridge, Proc. Nat. Acad. 14,788 (Oct., 1928).

previous measurement to a greater precision and a greater range of temperatures and currents. The present paper is a report of this work.

Apparatus and Methods

A diagram of the thermionic tube used is shown in Fig. 1. It was not essentially different from that used in the previous measurements,[5] except that the charcoal trap was replaced by an ionization gauge in which magnesium could be vaporized, and which served to measure the pressure and also to assist with the clean-up of the residual gases after the tube was sealed from the pumps. The filament of the present tube was mounted as shown so as to be more easily replaceable. It consisted of a platinum strip $2\times60\times0.01$ mm suspended along the axis of three coaxial nickel cylinders, the two outer ones acting as guard rings. The length of the central collecting cylinder, measured from center to center of the slits separating it from the guard rings, was 3.4 cm, so that the platinum surface from which emission was received was approximately 1.36 sq. cm. Connection of this cylinder to the electrometer was made through a well insulated seal coming directly out through the side of the tube in a direction at right angles to the plane of the figure.

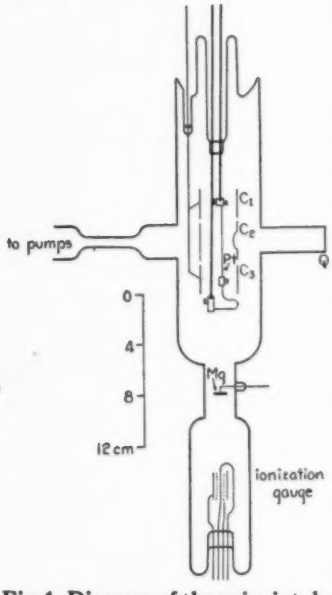

Fig. 1. Diagram of thermionic tube.

Outgassing process. After the installation of each new platinum specimen the whole tube was baked at 450–500°C for from 6 to 15 hours. The nickel cylinders were then heated to about 1300°C by high frequency induction until they no longer gave off appreciable amounts of gas. The grid and plate of the ionization gauge were given a thorough outgassing by bombardment. The whole tube was then rebaked for usually 24 hours and the cylinders again heated. During this time the platinum strip was kept glowing continuously at about 1300°C. After the above treatment the filament was kept at this temperature, with frequent periods at higher temperatures up to 1500°C, until the pressure as read by the ionization gauge was of the order of 10^{-8} mm with the strip hot, or until the thermionic emission from the platinum became nearly constant. The work function at this stage was usually about 6.0 volts. The magnesium disk was then heated by induction (having previously been outgassed) until a considerable quantity was vaporized throughout the tube; the tube was then carefully sealed off.* After several hours of heating of the strip with the ionization-gauge filament running at an emission of 10 milliamps. at 100 volts, the emission from the platinum reached a steady state and final measurements could then be taken.

It should be mentioned that only a small percentage of the platinum specimens installed survived the complete treatment. Some developed hot

* The author is indebted to Dr. J. A. Becker of the Bell Telephone Laboratories for helpful suggestions as to vacuum technique.

spots and soon melted at these points. A greater number simply broke for no apparent reason while at temperatures 400° below the melting point. This is probably caused by the recrystallization of platinum known to take place during long heating. The breaks occur even when the tension used to keep the filament straight is scarcely greater than the weight of the filament itself. However the occasional filaments which did withstand the outgassing process gave a beautifully consistent and reproducible emission.

Temperature measurements. The temperature of the platinum was measured by a Leeds & Northrup optical pyrometer focussed through the window *Q* whose absorption was known. The pyrometer was calibrated originally by the Bureau of Standards and was twice recalibrated in this laboratory by Dr. A. H. Warner and the author against a standard tungsten lamp which had been supplied to Dr. C. H. Prescott for his work[8] at this institute by Dr. Forsythe of the Nela Laboratories. All three calibrations were in agreement within 2° over the whole range.

The procedure in taking a run was at each successive value of the filament heating current to take simultaneous measurements of the temperature and thermionic emission,—making for each temperature measurement from six to twelve pyrometer settings. The measured temperatures, after being corrected for the emissivity of the platinum and the absorption of the window, were then plotted on a large sheet of graph paper as a function of the heating current. A smooth curve was drawn through the points, none of which fell off the curve by more than two degrees. The final temperatures were read from this curve and were therefore consistent among themselves for each run to better than one degree.

The emissivity of well-aged platinum as a function of temperature has recently been carefully measured by Worthing,[9] and his temperature scale was employed in the present work. It differs slightly from the earlier scale of Waidner and Burgess[10] and Mendenhall.[11] If the latter scale is used values of the work function are obtained which are about 1 percent lower than those given below. The discrepancy between the two scales is found particularly at the higher temperatures and Worthing gives evidence to indicate that considerable confidence may be placed in his measurements at these temperatures. However, as he himself says, the data for platinum are not completely satisfactory and this constitutes the chief source of error in the present experiments.

Emission measurements. Because of the high work function of platinum and the necessity of working at temperatures below 1750°K the emission currents were for the most part beyond the range of galvanometer measurements. Consequently a Compton electrometer shunted by a high resistance was used. Four such resistances were employed to enable a large range of currents (10^5 to 1) to be measured. They were mounted within the electrometer cage so that any one could be easily switched in by means of mercury

[8] Prescott and Hincke, Phys. Rev. **31**, 130 (1928).
[9] Worthing, Phys. Rev., **28**, 174 (1926).
[10] Waidner and Burgess, Bull. Bur. Standards, **3**, 163 (1907).
[11] Mendenhall, Astrophys. J., **33**, 91 (1911).

switches operated from outside. The three highest resistances were of India ink on drawing paper sealed in a tube of paraffin. The lowest was simply a metallic grid leak. Their values as determined by the time of leak across a standard condenser were 13,400, 1342, 68.8 and 2.58 megohms. The ratios between the successive resistances could also be accurately checked by measuring with them the same thermionic current. The need for more resistances of intermediate values was rendered unnecessary by the use of a null method of measuring. One end of the resistance in use was connected to the insulated quadrants and the other through a resistance box potentiometer to ground. The other electrometer quadrants were earthed directly. By means of the potentiometer the electrometer deflection could be brought to zero for each measurement, the potential required for this being of course just equal to the drop across the resistance due to the current being measured. The potentiometer readings in volts divided by the value of the resistance in ohms gave directly the thermionic current in amperes. By this means currents varying by a factor of nearly 500 could be easily measured with a single resistance. The potentials actually used varied from 0.01 to 1.0 volt and with the electrometer sensitivity used these could be determined to about 1/5000 volts, which is 2 percent of the smaller and 0.02 percent of the higher potential. However the smaller readings for each resistance were repeated with the next higher resistance with increased accuracy. On the other hand the slight unsteadiness in the filament heating current limited the accuracy of the higher potential measurements to about 0.1 percent so that on the whole the potentiometer readings were consistent to better than one-half percent. The errors in the measurements of the resistances themselves were also of about this order of magnitude.

To obtain the above degree of steadiness (0.1 percent) in the thermionic currents the heating current through the strip had to be kept constant to 1 part in 5000. This was accomplished by using two 20-volt banks of large storage cells in parallel and a series of fixed constantan resistances which could be easily switched in and out, all shunted by a good high resistance rheostat for fine adjustment. The current passed through a 0.1 ohm standard resistance and was measured by a potentiometer and standard cell. The resistances were so arranged that by proper manipulation the heating current could be set and maintained at any desired value within the limits required. It was kept at each value for several minutes before readings were taken to insure complete thermal equilibrium.

Schottky effect. In order to correct the values of b and A for the effect of the accelerating potential, V, between the filament and cylinders the Schottky equation was used. This may be written,

$$\Delta b = 2.303T(d \log_{10} I/dV^{1/2})V^{1/2}.$$

The value of the derivative is obtained by plotting the logarithm of the thermionic current as a function of the square root of the potential V, and determining the slope of the resulting straight line. Such a plot for a temperature of 1618°K is shown in Fig. 2. From this we calculate, $\Delta b = 370$°K approximately, for $V = 132$ volts, the value used in the measurements given below. This is in good agreement with the values obtained for other temperatures.

Results

As is usual in such measurements the value of the work function was determined from the slope of the straight line obtained by plotting (log I/T^2) as a function of $1/T$. The value of b so obtained is then used to calculate log A for each reading. The constancy of the values of A obtained for various temperatures is a test of the consistency of the emission and temperature readings. The measurements and calculations for one of the best runs obtained are summarized in Table I and Fig. 3. The first three columns of the table give, respectively, the filament heating current, the emission current reduced to amp/cm², and the true temperature of the strip. The next two columns give data used in plotting the curve. The sixth column gives the calculated values of $b/2.3T$, using for b the slope of the curve of Fig. 3. The last column gives the values of log A obtained by adding the values in column 6 to the corresponding values in column 4. It will be noted that the measurements extend over a range of temperature of nearly 400° which is about the maximum that can be conveniently obtained for platinum, and that the values of the emission current vary over a factor of over 10^5.

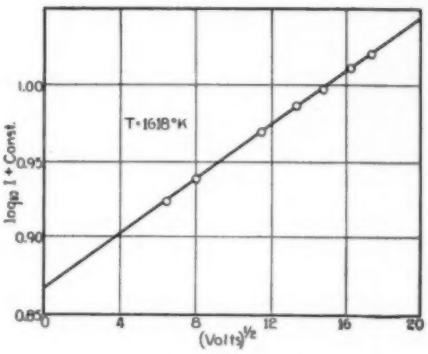

Fig. 2. The Schottky effect.

Table I. *Thermionic Emission data for Pt.*

b (from slope) = 72,450°K. V = 132 Volts.

I	II	III	IV	V	VI	VII
Heating Curr. amp.	$I\times10^{11}$ amp/cm²	T °K	$\log_{10} I/T^2$ +19	$1/T$ $\times10^7$	$b/2.3T$	$\log_{10} A$
3.1	0.0406	1367	0.337	7315	23.02	4.357
3.3	0.152	1406	0.887	7112	22.38	4.267
3.5	0.607	1444	1.467	6925	21.79	4.257
3.7	2.07	1480	1.977	6757	21.26	4.237
3.9	6.91	1515	2.478	6601	20.77	4.248
4.1	21.25	1549	2.946	6456	20.32	4.266
4.3	61.20	1583	3.387	6317	19.88	4.267
4.5	164.0	1618	3.795	6180	19.45	4.245
4.7	410.3	1651	4.178	6061	19.065	4.243
4.9	1000.	1683	4.546	5942	18.70	4.246
5.1	2322.	1715	4.896	5831	18.35	4.246
5.3	4470.	1745	5.229	5731	18.035	4.254
					Average	4.252

The points when plotted as in Fig. 3 fit the straight line relation very accurately, no point being further off than could be accounted for by an error in the temperature of 0.5°. The value of b obtained from the slope is 72,450°K. Using this value for b the average value of log A as shown in the last column is 4.252, corresponding to $A = 17{,}850$ amp/cm² deg². Aside from the first reading for which the thermionic current was too small to be measured accurately, the maximum deviation from the mean value of log A is 0.37 percent corresponding to a 3.5 percent deviation in A itself which must

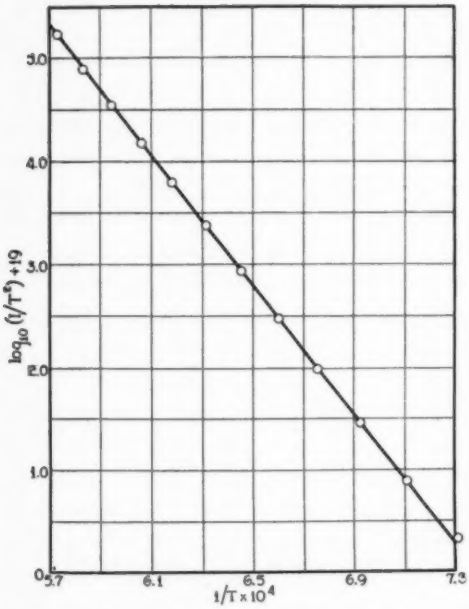

Fig. 3. Thermionic curve for clean platinum.

be considered a very satisfactory agreement. When corrected for the Schottky effect, the values obtained are

$b = 72{,}820°K$

$\phi = bk/e = 6.27$ volts.

$A = 17{,}000$ amp/cm^2 deg^2, approx.

The above values were obtained under very good conditions and are good averages of the results obtained in many other runs on various specimens of platinum. They are believed to be close to the true values for the clean metal. It will be noted that the value for ϕ is slightly less than that given by the previous less precise measurements[12] ($6.35 \pm .1$ volts) though it is within the limits of error of those measurements. Due to the greater precision the present value is probably more reliable. It is in even better agreement with the value 6.30 volts previously obtained for the photoelectric work function. Assuming the correctness of the Worthing temperature scale the above value for ϕ should not be in error by more than 0.5 percent. Because of this uncertainty however the error may be 1 percent or slightly more, so that the best value of the work function given by the present data is $\phi = 6.27 \pm 0.07$ volts.

It is impossible to be certain of the value of A to better than possibly 25 percent. However it is clear that the value obtained is at least 250 times greater than the theoretical value of 60.2 observed for other metals. If the value $A = 60.2$ be assumed and b calculated from the data we find,

for $T = 1406°K$, $b = 64{,}500°K$; $T = 1651°$, $b = 63{,}300°$; $T = 1745°$, $b = 62{,}500°$,

which do not agree with each other and which differ from the value given by the slope of the curve by from 11 to 14 percent. The value 60.2 thus cannot possibly be reconciled with the present measurements. Bridgman[13] has shown that the observed value of A can be accounted for without doing violence to the otherwise satisfactory theories of thermionic emission by the very simple assumption that the surface work function (photoelectric) varies slightly with temperature. This theory and its relation to the present results and to the variations in A *during* outgassing have been discussed in another paper.[7]

The author is indebted to Dr. Millikan and the staff of the Norman Bridge Laboratory for the facilities placed at his disposal.

California Institute of Technology,
August 20, 1928.

[12] There is an unfortunate error in labelling the ordinates of Fig. 3 of the second paper of reference 5. These numbers should read 0.8, 1.6 and 2.4 instead of .4, .8, and 1.0 resp.

[13] Bridgman, Phys. Rev., 31, 862 (1928).

ELECTRICAL RESISTANCE AND MAGNETIC PERMEABILITY OF IRON WIRE AT RADIO FREQUENCIES*

By G. R. Wait, F. G. Brickwedde, and E. L. Hall

Abstract

The magnetic permeability of iron wire at high frequencies.—G. R. Wait, investigating the magnetic permeability of iron and magnetite in high frequency magnetic fields, did not observe a critical variation of the permeability at about 3000 kilocycles (100 meters wave-length) as reported by Wwedensky and Theodortschik. It was suggested that the difference in the results might have been due to: (1) a difference in the kinds of iron investigated; (2) a difference in the strengths of the magnetic fields; and (3) a difference in the manner of suspending the iron sample. A sample of iron wire in which critical variations had been observed by Kartschagin and by Mitiaev was used in the present investigation with the same apparatus as had previously been used by Wait. Experiments were carried out in a magnetic field of an intensity equal to 0.5 gauss, as previously used by Wait, and also in a field of 0.01 gauss, the intensity of the field in which Wwedensky and Theodortschik observed the critical variation. Different methods of binding the sample were also tried. In no case was a critical variation in permeability observed.

The electrical resistance of iron wire at high frequencies.—Mitiaev observed that the resistance of iron wire to a high-frequency current and its internal self-inductance underwent a critical variation at about 3000 kilocycles. Calculations of the permeability involving these quantities gave results in substantial agreement with those of Wwedensky and Theodortschik on the variation of permeability with frequency. The resistances of iron wires intermediate in size between those used by Mitiaev were measured by the resistance-variation method as described in Bureau of Standards Circular 74. The investigation was carried out between 4300 and 2500 kilocycles (70 and 120 meters wave-length). No critical change within the limits of observable accuracy was detected.

The Magnetic Permeability of Iron at Radio Frequencies

THE magnetic permeability of iron, steel, and nickel in oscillating magnetic fields was observed by Wwedensky and Theodortschik[1] to undergo a critical variation at about a frequency of 3000 kilocycles† (100 meters wave-length). This was attributed to resonance, with the alternating magnetic field of vibrating elementary magnets, of which the ferro-magnetic substances were supposed to be constituted. The phenomenon was later studied by G. R. Wait[2] who made use of two of the methods used by Wwedensky and Theodortschik. With improved apparatus, resulting in greater accuracy,

* Published with the approval of the Director of the Bureau of Standards and the Director of the Department of Terrestrial Magnetism of the Carnegie Institution of Washington.

† In the present communication we have used frequencies expressed in kilocycles per second instead of meters wave-length, but have plotted our results using meters wave-length in order that they might be more easily compared with all the previous work on this subject in which the writers used wave-lengths instead of frequencies.

[1] B. Wwedensky and K. Theodortschik, Ann. d. Physik **68**, 463 (1922), and Phys. Zeits. **24**, 216 (1923).

[2] G. R. Wait, Phys. Rev. **29**, 566 (1927).

no critical variation in permeability was observed. The problem being one dealing with the fundamental nature of the structure of magnetic materials, it was considered of sufficient importance to warrant further study, particularly in an effort to explain the difference between the results of these two investigations.

In this investigation Wait's apparatus was used, and for a complete description and method of using it, as well as for the computation of results, the reader is referred to his original paper.[2] Briefly, two loosely coupled electron-tube oscillators, *A* and *B* of Fig. 1, were tuned so as to give a small number of beats per second which were detected by means of an audio-frequency amplifier. The sample under investigation, upon being introduced into the coils of set *B*, increased their inductance, thereby changing the pitch

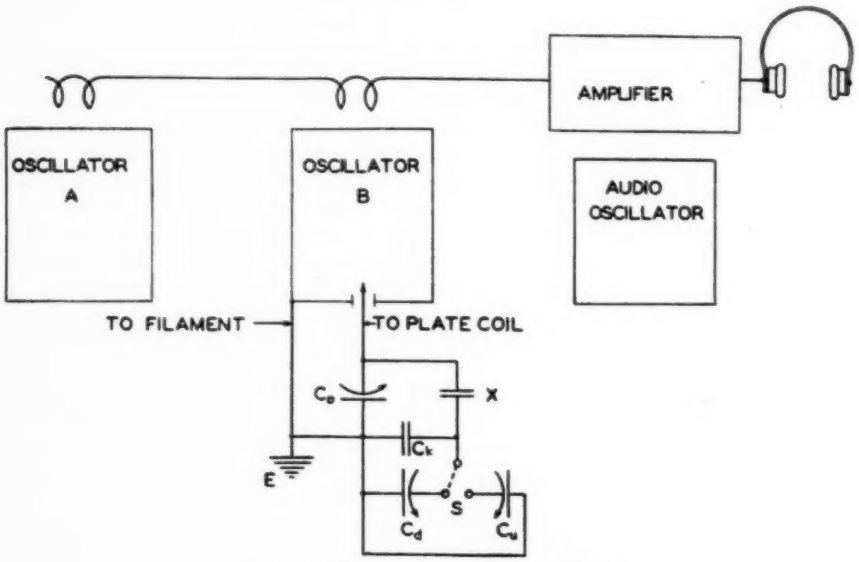

Fig. 1. Diagrammatic sketch of apparatus.

of the beat-note. This change in inductance was compensated for by a change ΔC_d in the capacity of the circuit, which thus brought back the original beat-note. The oscillators *A* and *B* and their condensers were shielded electrically by separate brass boxes, the batteries and the amplifying unit were enclosed in wooden boxes covered by sheet metal, and all exterior electrical connections were covered by metal tubes. For this investigation the apparatus was improved by shortening to a minimum the electrical connections between condensers and between them and the oscillators.

It was suggested that the difference between the results of Wwedensky and Theodortschik and those of Wait may have been due to one or more of the following differences between the two investigations: (1) A difference in the kinds of iron used; (2) a difference in the strengths of the magnetic fields; (3) a difference in the manner of suspending the iron samples.

Professor Arkadiew very kindly supplied us with a sample of iron wire used by Kartschagin[3] and Mitiaev[4] in which critical variations were observed by them. With this wire the experiments were carried out in a magnetic field of an intensity equal to 0.5 gauss, the same as that previously used by Wait, and also in a field of the same intensity, namely 0.01 gauss, as that in which Wwedensky and Theodortschik observed the critical variation. In those experiments using a field of 0.01 gauss, the sample was placed in the weaker regions of the coil's magnetic field where the intensity was of the desired value.

It was suggested that we try the experiment with the wires composing the sample secured so as not greatly to interfere with possible mechanical vibra-

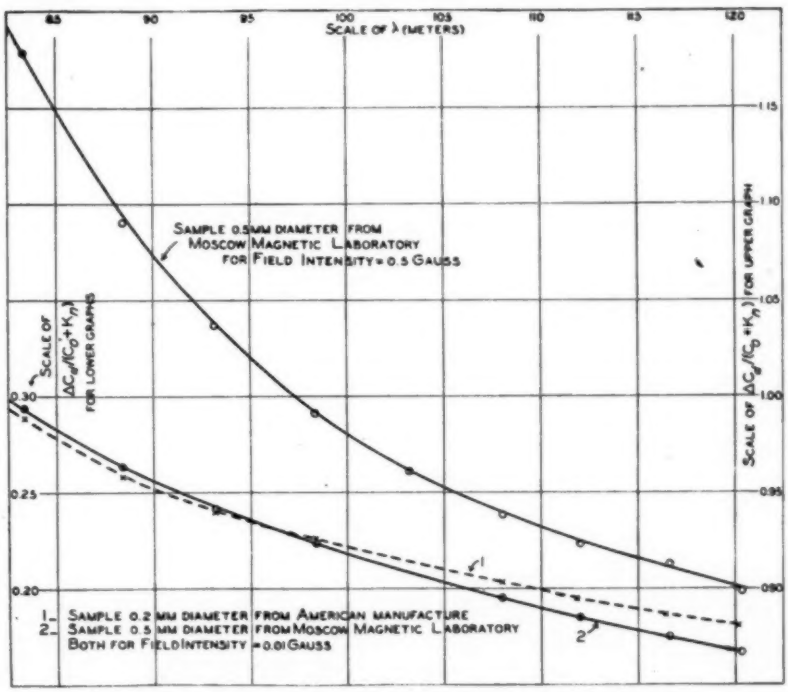
SCALE OF λ (METERS)
SAMPLE 0.5 MM DIAMETER FROM MOSCOW MAGNETIC LABORATORY FOR FIELD INTENSITY = 0.5 GAUSS
SCALE OF ΔC_d/(C_0+K_n) FOR LOWER GRAPHS
SCALE OF ΔC_d/(C_0+K_n) FOR UPPER GRAPH
1 SAMPLE 0.2 MM DIAMETER FROM AMERICAN MANUFACTURE
2 SAMPLE 0.5 MM DIAMETER FROM MOSCOW MAGNETIC LABORATORY
BOTH FOR FIELD INTENSITY = 0.01 GAUSS

Fig. 2. Permeability of soft iron wire by beat-method.

tions. This was done by placing the strands in separate tubes of electrical "spaghetti," in which they were secured with a little paraffin at the lower end, the tubes being bound loosely into a bundle.

The results of the investigation on the wire furnished by Professor Arkadiew at field strengths of 0.5 and 0.01 gauss, and also on a sample of American wire are shown in Fig. 2.

Beltz[5] showed that if a substance with volume V', having a sufficiently small susceptibility κ and correspondingly permeability μ, is introduced into

[3] W. Kartschagin, Ann. d. Physik **67**, 325 (1922).
[4] W. K. Mitiaev, Zeits. f. Physik **38**, 716 (1926).
[5] M. H. Beltz, Proc. Cambridge Phil. Soc. **21**, 52 (1922); Phil. Mag. **44**, 479 (1922).

an oscillating coil of volume V and inductance L, and if the inductance of the coil is altered by an amount ΔL, then, neglecting effects arising from eddy-currents, demagnetization, end-effects of the sample, and an alteration in the magnitude of the field due to the presence of the interior shield,

$$(V/V')(\Delta C/C)=(V/V')(\Delta L/L)=4\pi\kappa=\mu-1$$

where C $(=C_0+K_n)$ is the capacity of the system and ΔC $(=\Delta C_d)$ the change in capacity necessary to compensate for the change in inductance. Wwedensky and Theodortschik applied this formula to their results to get a quantity termed "apparent permeability." In the present paper, to make proper

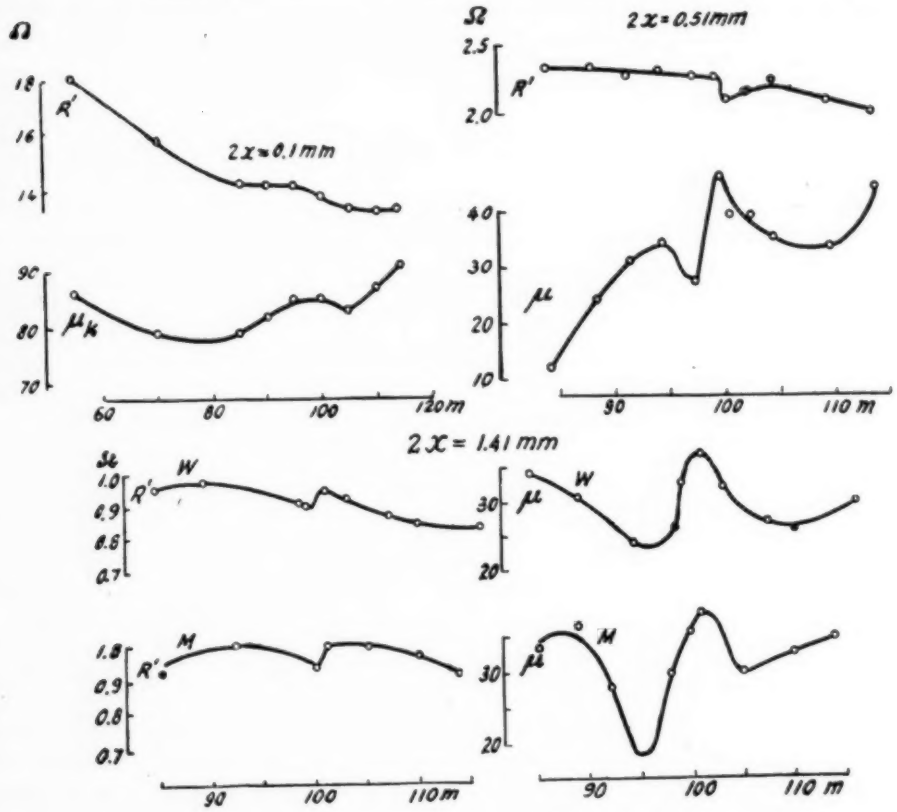

Fig. 3. Some results of Mitiaev and Wwedensky.

comparison with the results of others, the quantity $\Delta C_d/(C_0+K_n)$ has been plotted against λ, the wave-length in meters. A critical variation, then, in permeability will be shown up as an irregularity in the curves as plotted. As they show no irregularities, they substantiate the results previously reported by Wait.

Electrical Resistance of Iron Wire at Radio Frequencies

W. K. Mitiaev[4] observed that the electrical resistance and internal self-inductance of iron wire to a radio-frequency current underwent a critical

variation at a frequency of about 3000 kilocycles (100 meters wave-length). By means of a formula involving the internal self-inductance and the radio-frequency and direct-current resistances of the wire, he calculated its permeability. This independent method of determining permeability gave results in substantial agreement with those of Wwedensky and Theodortschik, using the beat-method, that is, the permeability was observed to undergo a critical variation at a frequency of 3000 kilocycles (100 meters wave-length). These results on resistance R', and permeability μ, are shown graphically in curves of Fig. 3, taken from Mitiaev's paper. The observed resistance in ohms and the calculated permeabilities are plotted against wave-lengths in meters for wires of three different diameters, $2x$. The curves marked with the letter W are taken from results obtained by Wwedensky in 1924, which Mitiaev reported in his paper, the other curves being Mitiaev's own results. In view of the contradictory results of Wait on permeability and also because of the importance of the electrical-resistance problem itself, it was decided to investigate the variation of resistance with frequency in this region.

The resistance of the iron wire carrying the radio-frequency current was determined by the resistance-variation method as described in Bureau of Standards Circular No. 74 (pp. 180–184). A diagram of the electrical connections of the apparatus is shown in Fig. 4. The source of the radio waves was a 250-watt electron-tube radio-frequency generator employing the tuned-plate type of circuit. This generator was used in the Radio Laboratory of the Bureau of Standards for the calibration and testing of radio instruments. In this investigation, however, only a small fraction of the power of this tube was used, actually less than 5 watts, the filament and plate-voltages being 16 and 300 volts, respectively. Radio waves of the desired frequency were received by the coil B, wound with the iron wire whose resistance was being investigated. The induced current flowed through the variable condenser C, the thermo-ammeter (consisting of thermo-element T and sensitive Weston galvanometer G), and through a resistance-link inserted across the gap A. These resistance links were of the standard radio-frequency type, the resistance-variation with frequency being negligible. They were made by sealing in a protecting glass tube a short straight thread of fine constantan wire soldered between two heavier copper wires whose amalgamated ends projected from the tube and dipped into mercury cups. These resistance-links included a copper link of practically zero resistance made from heavy copper wire, in all other respects like the constantan links, all links being alike in size so that the replacing of one by another caused no change in the

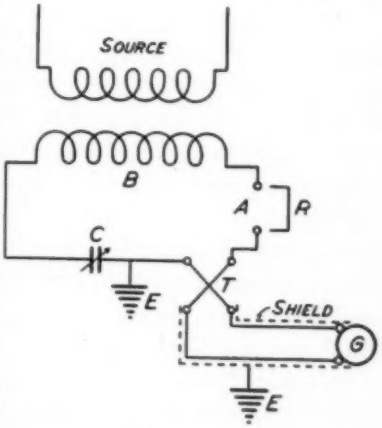

Fig. 4. Apparatus for measuring electrical resistance of iron wire at radio frequencies.

inductance of the circuit. The resistance of the circuit—which, other than that of the thermo-element amounting to 2.87 ohms, was due almost entirely to the iron coil—was found by determining the currents which flowed through the circuit (1) I_0, when the copper link of zero resistance was inserted across the gap A, and (2) I_1, when the copper link was replaced by a constantan link of known resistance, R_1. From these determinations the resistance R of the circuit was calculated by means of the formula, $R=R_1/(I_0/I_1-1)$. In practice, however, four constantan links were used and the resistance, R, calculated for each.

The procedure of the experiment was as follows: The generator was set at approximately the desired frequency, the receiving circuit was tuned and its frequency determined. The resistance-links were inserted and galvanometer deflections read for the resistances in the order inserted: 0.00, R_1, R_2, R_3, R_4, R_4, R_3, R_2, R_1, 0.00, galvanometer-zeros for open circuit being observed before and after the insertion of each link. Finally, the frequency of the generator was checked to make certain there had been no drift during the measurements. The resistances were inserted in rapid succession and remained in the circuit only long enough to allow the deflections to be read, the receiving circuit being kept open at all other times to prevent unnecessary heating of the thermo-element.

The galvanometer and thermo-element were calibrated with a 60-cycle alternating current. The frequency meter used was one of those employed by the Bureau of Standards for calibrating and testing radio instruments. The receiving apparatus was shielded from the observer's body, the condenser and thermo-element were enclosed in metal cases, and the leads to the galvanometer were drawn through a grounded copper sheath. The accuracy of measurements were such that in only a few cases did the separate determinations of the resistance of the circuit, using the four different constantan links, vary from the mean by more than one percent.

The method we have used is essentially the same as that used by Mitiaev.[4] He, however, used a pick-up coil in series with a rectangular frame of iron wire, which was short-circuited in some determinations. This procedure undoubtedly caused a change in the induced electromotive force which was not, however, taken into consideration in the computations. Mitiaev, by his method determined not only the resistance of the iron wire, but also its internal self-inductance, which thus enabled him to compute the permeability. We sought to determine the resistance more accurately. Further, in the method used in this investigation, the electromotive force of the circuit was constant throughout the set of readings taken at each frequency, provided, of course, the power-output of the generator remained constant. The checking of the current with the copper link of zero resistance at the beginning and at the end of each set of observations showed that this did remain constant. The method used did not, however, permit a determination of the internal self-inductance of the iron wire with sufficient accuracy to warrant a calculation of its permeability.

In Fig. 5 are shown our results for two samples of American iron wire, 1.2 mm and 0.2 mm in diameter. The resistances are plotted as ordinates against wave-lengths as abscissas. Three independent sets of observations were made on the large-size wire and the lower curve of the diagram represents the average of these three determinations. On the smaller wire only one set of observations was made and the results are shown in the upper curve. The radii of the circles surrounding the observed points of the two graphs represent one percent of the mean value of the resistance for each of the two wires. The curves show no critical variation. We conclude, therefore, that within the accuracy of the experiments there is no critical variation of the resistance at the frequencies investigated. The critical variation observed

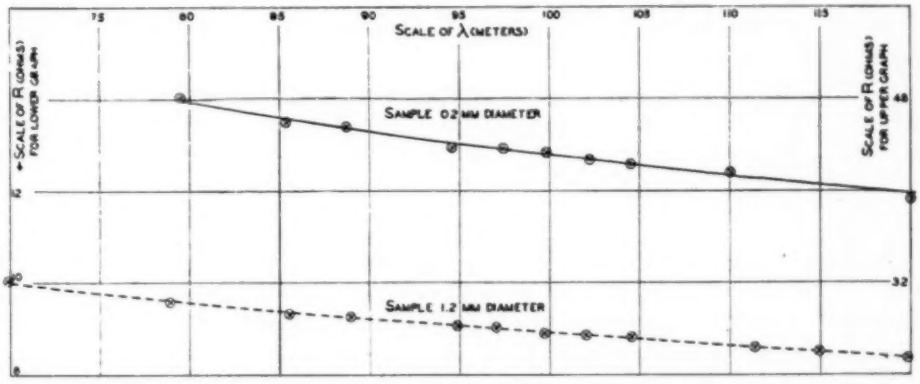

Fig. 5. Electrical resistance at radio frequencies of soft iron wire of American manufacture.

by Mitiaev at 3000 kilocycles (100 meters wave-length was a departure from the mean of between 4 and 7 percent. Since Mitiaev's experimental error, as stated in his paper, was about 2 or 3 percent, our investigation was more favorable than his for the detection of any critical variation that might exist. Since the wires used in the present investigation were intermediate in size between those used by Mitiaev, it is unlikely that the difference between the results of the investigations can be ascribed to a difference in the size of wires.

A failure to detect a critical variation in the resistance of iron wire to a radio-frequency current at frequencies in the vicinity of 3000 kilocycles is regarded as further confirmation of the earlier results of Wait[2] and those of the first part of the present paper on permeability, that is, that there is no critical variation in permeability of iron wire at a frequency of 3000 kilocycles (100 meters wave-length).

The authors take advantage of this opportunity to express their appreciation to Mr. J. A. Fleming for his interest and help in this investigation and especially to Dr. G. Breit for valuable advice and assistance.

CARNEGIE INSTITUTION OF WASHINGTON (G. R. W.).
BUREAU OF STANDARDS (F. G. B. and E. L. H.).
September 5, 1928.

ON FREE AND BOUND ELECTRONS IN METALS

By Richard Ruedy

Abstract

When the theory of dispersion in an absorbing medium is applied to the values published in recent years for the optical properties of different metals, it follows that bound electrons exist inside the metal comparable in number with that of the free electrons.

IN THEIR new theory of the electric conductivity of metals, Sommerfeld, Houston and Eckart did not have to examine "the essential problem of the degree of dissociation of the metal i.e. the number of free electrons per atom."[1] It is known that if the conductivity of the metallic elements be plotted as a function of the atomic number, the curve obtained shows marked peaks at the beginning of each period or half period (Cu, Ag, Au) and an irregular drop toward the end of the period. With an increasing number of valency electrons the conductivity seems to decrease, and those elements having in their atomic configuration one single outermost electron possess the highest conductivity. Only three elements were an exception when this rule was first observed: Cr, Mo, W, which attain new high values inside their period.[2] But the analysis of their spectra has since shown that these atoms too possess one outermost electron in an uncompleted shell, or that one single electron plays an important part in the emission and absorption of light. Even if instead of this rough comparison the elements are examined at corresponding temperatures and with the same field applied per atom, so as to eliminate as far as possible the influence of crystalline structure, the dependence of the conductivity upon the number of outer electrons is still well marked.[3] It may therefore be assumed that the number of free electrons is about equal to the number of valency electrons.

On the other hand the electric conductivity of the metal is closely connected with its optical properties. The reflective power in the far infra-red region, for example, may be calculated from the specific conductivity of the metal.[4] The better the conductivity, the stronger is the absorption. Down to wave-lengths larger than about 4μ, the metals behave optically as if they contained only free electrons. In the visible spectrum, however, there appear signs of bound electrons which are set into vibration by the incident light waves. We may try to find the relative number of free and bound electrons from a study of the optical properties of the metal in the visible and ultra-violet spectrum. In recent years some new measurements have been published

[1] A. Sommerfeld, Zeits. f. Physik. **47**, 1 (1928); W. V. Houston, Zeits. f. Physik. **47**, 33 (1928); C. Eckart, Zeits. f. Physik. **48**, 449 (1928); A. Sommerfeld, Naturwiss. **16**, 374 (1928).

[2] O. Feussner, Zeits. f. Physik. **25**, 215 (1924).

[3] H. Cassel, Zeits. f. Physik. **33**, 477 (1925).

[4] R. W. Wood, Physical Optics.

on this interesting but difficult problem, and it seems worth while to examine the results from the point of view of the theory of dispersion and absorption.[5]

The general equation for dispersion and absorption is

$$n^2(1-i\kappa)^2=1+\sum\frac{\zeta/4\pi^2}{\nu_0^2+i\nu\nu'-\nu^2} \tag{1}$$

where $(2\pi\nu_0)^2=4\pi e^2f/m=4\pi f/m'$; N is the number of electrons of frequency ν_0 per unit volume; ν_0 the natural frequency of the electrons; f the elastic force (at 1 cm distance) calling the electron to its equilibrium position; $\nu'=r/2\pi m'$ where r is the friction met with by the electrons in crossing the metal; and $\zeta=4\pi Ne(e/m)=4\pi N/m'$.

Separating the imaginary and real quantities and introducing $\lambda=c/\nu$, this equation becomes

$$2n^2\kappa=\sum\frac{\zeta/4\pi^2c^2\lambda\lambda'}{(1/\lambda_0^2-1/\lambda^2)^2+1/\lambda^2\lambda'^2}=\sum\frac{C/\lambda\lambda'}{(1/\lambda_0^2-1/\lambda^2)^2+1/\lambda^2\lambda'^2}$$

$$n^2(1-\kappa^2)-1=\sum\frac{\zeta/4\pi^2c^2\times(1/\lambda_0^2-1/\lambda^2)}{(1/\lambda_0^2-1/\lambda^2)^2+1/\lambda^2\lambda'^2}=\sum\frac{C(1/\lambda_0^2-1/\lambda^2)}{(1/\lambda_0^2-1/\lambda^2)^2+1/\lambda^2\lambda'^2}$$

If the substance considered possesses one class of free electrons ($\nu_0=0$) besides "i" groups of bound electrons, its optical properties will be determined by

$$2n^2\kappa=\underset{\text{(free electrons)}}{\frac{C\lambda'\lambda^3}{\lambda^2+\lambda'^2}}+\underset{\text{(bound electrons)}}{\sum_0^i\frac{C_i/\lambda\lambda_i'}{(1/\lambda_i^2-1/\lambda^2)^2+1/\lambda^2\lambda_i'^2}} \tag{2}$$

$$n^2(1-\kappa^2)-1=-\frac{C\lambda'^2\lambda^2}{\lambda^2+\lambda'^2}+\sum_0^i\frac{C_i(1/\lambda_i^2-1/\lambda^2)}{(1/\lambda_i^2-1/\lambda^2)^2+1/\lambda^2\lambda_i'^2} \tag{3}$$

The values of C and C_i are subject to the condition that they yield a sum corresponding with the total number of valency electrons inside unit volume of the metal:

	Cu	Ag	Au (one electron per atom)	Na	Ni (two electrons per atom)	Hg
$N\times10^{-22}$	8.5	5.6	6	2.5	18	6.2
C	0.8	0.5	0.5	0.2	1.6	0.6

λ being expressed in 10^3AU.

If the value of the incident wave-length λ exceeds λ' as well as λ_i and λ_i'

$$2n^2\kappa=C'\lambda'=2\pi cm'C'/r \text{ or } n^2\kappa=N'/r\nu$$

N'/r may be interpreted as the electric conductivity σ of the metal, and for many metals Hagen and Rubens[6] have established (large λ)

[5] G. Pfestorf, Ann. d. Physik **81**, 906 (1926); K. Lauch, Ann. d. Physik **74**, 55 (1924); J. Richter, Ann. d. Physik **77**, 81 (1925). See also W. Meier, Ann. d. Physik **31**, 1017 (1910).

[6] E. Hagen and H. Rubens, Ann. d. Physik **11**, 873 (1903).

$$n^2\kappa=\sigma/\nu$$

We may then deduce a minimum value for $\lambda'=2\pi m'c/r$ by supposing all the electrons inside the metal as free; this gives (in A.U.$\times 10^{-3}$).

Cu,	538;	Ag,	705;	Au,	535; with one electron per atom
Ni,	29.5;	Hg,	8.5;	Pt,	54; with two electrons per atom

For the large values of λ', the well known relation $n^2\kappa=\sigma/\nu$ ceases to be quite accurate; and besides, the new theory of conductivity does not confirm fully the expression $\sigma=N'/r$. The exact value of λ', however, is rather indifferent as long as it is large. Another feature for large λ' is that in the visible

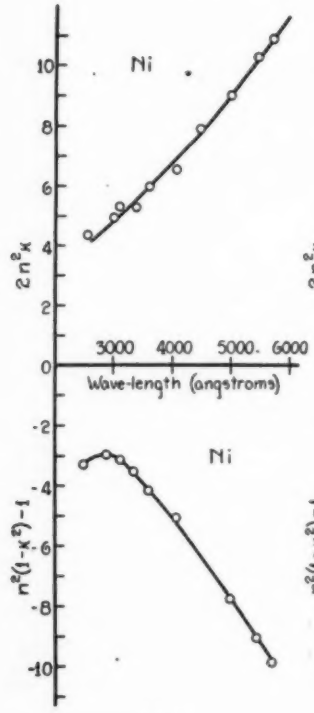

Fig. 1.

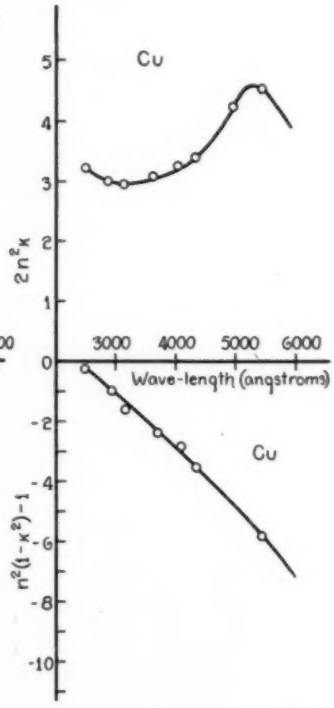

Fig. 2.

spectrum the contribution to the value of $2n^2\kappa$ by the free electrons will be small or negligible, so that the presence of bound electrons becomes at once apparent. The part of the free electrons in determining $n^2(1-\kappa^2)$, on the other hand, is well marked, independent of λ' and therefore similar for all good conductors. The presence of free electrons alone causes a steady decrease for $n^2(1-\kappa^2)$ and a steady increase in the value of $2n^2\kappa$, as the wave-length increases. Therefore a graph (Figs. 1 and 2) representing $2n^2\kappa$ and $n^2(1-\kappa^2)$ as a function of the wave-length of the incident light, indicates clearly the regions where bound electrons and the regions where free electrons have a prominent part in determining the optical constants of the metal, and suggests approxi-

mate values for C, λ' and λ as used above. By comparing the new experimental results for Cu, Au and Ni with a sufficient number of theoretical curves calculated from Eqs. (2) and (3), values for C, λ and λ' may be picked out (Table I), which by means of Eqs. (2) and (3) determine the optical properties of these metals within the limit of experimental errors (Table II). In the tables, p_0 is the average number of free electrons per atom, p_1 and p_2 are the average number of bound electrons having natural frequencies corresponding with λ_1 and λ_2 and the values λ_1' and λ_2' as defined above, λ being given in 10^3 A.U.

TABLE I. *Calculated values of C, λ and λ'.*

Metal	Free electrons p_0	λ'	C	Bound electrons 1st kind p_1	λ_1	λ'_1	C_1	2nd kind p_1	λ_2	λ_2'	C_2	λ_3
Cu	0.3	large	0.25	0.1	5.2	10	0.08	0.75	2.0	2	0.6	
Ag	.6	large	.3					.8	2.2	4	.4	
(old values)												
Au	.6	large	.3	.05	5.2	10	.05	.6	3.0	6	(.3)	(1.5)
Ni	.45	7.5	.7					.45	2.0	2	.7	

TABLE II. *Optical constants of Ni, Cu, Au.*

		λ=	3	4	5	6
Ni	$2n^2\kappa$	obs	5.0	6.5	9.0	12.3
		calc.	4.3	6.2	9.3	12.6
	$n^2(1-\kappa^2)-1$	obs.	−3.1	−5.0	−8.0	−11.0
		calc.	−3.9	−6.2	−9.1	−11.5
Cu	$2n^2\kappa$	obs.	2.9	3.2	4.2	3.8
		calc.	2.5	2.8	4.8	4.6
	$n^2(1-\kappa^2)-1$	obs.	−1.2	−2.8	−4.9	−7.2
		calc.	− .6	−3.4	−4.5	−6.8
Au	$2n^2\kappa$	obs.	5.5	3.4	4.0	2.4
		calc.	5.6	3.7	4.1	3.4
	$n^2(1-\kappa^2)-1$	obs.	− .1	−1.6	−7.8	−8.8

The values n and κ are usually certain to ± 0.04 or ± 0.05 units; this causes an uncertainty of 0.8 to 1.2 in the values of $2n^2\kappa$ and $n^2(1-\kappa^2)$. More accurate figures could only be obtained by taking a very large number of readings so as to eliminate the small accidents upon the metallic surface due to the polishing and treatment of the metal. The values for the natural frequencies below $200\mu\mu$ are not reliable, as no readings in this region exist, where the influence of the ν's would appear most plainly. A large number of metals must possess a band at or below $200\mu\mu$ which is decisive for the optical properties. Cu and Au alone appear to have a band of natural frequencies in the visible spectrum; but it comes from a comparatively small number of electrons and may correspond with a forbidden transition. In contrast with Ag, the spectrum of which is almost exclusively due to the single valency electron, Au and Cu atoms show a system of lines built up upon a metastable level.

Sommerfeld has pointed out as a consequence of the Pauli-Fermi distribution of energy, that the electrons in the interior of a metal possess a much

higher kinetic energy than would be expected from the older equipartition theory. The kinetic energy per electron, if all the electrons in the volume V or only half the electrons are free, follows from

$$W_0=\frac{3h^2}{40m}\left(\frac{6N}{\pi V}\right)^{2/3}$$

as follows:

for	Cu	Ag	Au	Na	Hg	Ni	
	5.5	3.4	3.6	2	3.6	7.5	Volts
or	3.3	2.1	2.3	1.3	2.2	4.7	Volts

Ag perhaps excepted, these values for the kinetic energy allow bound electrons to be present in the metal, having natural frequencies corresponding with the visible or ultra-violet spectrum. For an accurate comparison it would be necessary to know the influence of the high density of the metal upon its dispersion and absorption.[7]

If the conductivities of the metals are now calculated from Houston's formula, assuming one half of the number of the valency electrons to be free, the agreement with the experimental values becomes better than before. This is the more remarkable as the classical theory of the diffraction of x-rays used in establishing the formula is not well supported by experiment: the influence of temperature having always been found larger than predicted.

The more recent values obtained for the absorption and dispersion of light by metals confirm the older ones in that they require for their explanation the existence of bound electrons inside the metal comparable in number with that of the free electrons.[8]

UNIVERSITY OF TORONTO.
July, 1928.

[7] K. F. Herzfeld, Phys. Rev. **29**, 701 (1927).

[8] The magnetic properties of single crystals of Zn and Cd, which have recently been studied at my suggestion, and the magnetic susceptibilities of the alkali metals point also to the existence of a certain proportion of bound and shared electrons (Nature **121**, 351 (1928).

ANOMALOUS DISPERSION, ABSORPTION AND KERR EFFECT IN VISCOUS DIELECTRICS

By Donald W. Kitchin and Hans Müller*

Abstract

The *temperature variation of the dielectric constant* and *power factor* of castor oil and rosin, measured at different frequencies from 10^7 to 60 cycles, shows that, in accordance with Debye's theory of polar molecules, the region of anomalous dispersion of these very viscous liquids shifts with decreasing temperatures into the long-wave radio region and even down to audio frequencies. The measurements qualitatively verify the theory. The *influence of viscosity* in solutions of rosin in different oils which have no polar molecules is found in agreement with the theory. The existence of anomalous dispersion in the audio and radio frequency region explains the complicated dielectric behavior of many insulation materials and makes it possible to observe an anomalous behavior of the Kerr effect, or electric double refraction. According to Debye, this effect is due to the orientation of the molecules and should disappear at temperatures and frequencies where the orientation of the dipoles is impossible. We find, as is to be expected, that the regions of anomalous Kerr effect and of anomalous dispersion coincide.

MEASUREMENTS of the dielectric constant δ and of the power factor f of rosin and castor oil, carried out for engineering purposes, led to curious results which, we believe, represent an interesting contribution to Debye's theory of polar molecules.

Experimental Method

The experimental arrangement is represented in Fig. 1. A resonant circuit is coupled to a calibrated oscillator, using a 201A tube. The test condenser consisted of two coaxial cylinders. Experiments showed that its vacuum capacity C_v did not vary with temperature.

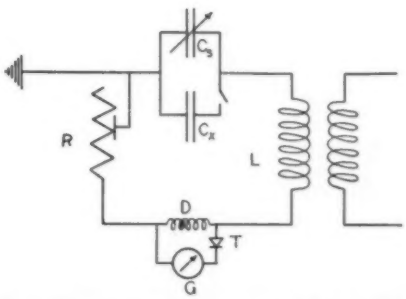

Fig. 1. Experimental arrangement. C_s is the variable standard condenser; C_x, the test condenser; R, the variable resistance; L, inductance; D, drop coil; G, micro-ammeter; T, the crystal rectifier.

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Each run was made at constant frequency and varying temperature. The method consisted of tuning the circuit to resonance with C_x connected and $R=0$, and noting the galvanometer deflection. Then, with C_x disconnected, the circuit was again brought to resonance and R varied to bring the galvanometer to the same deflection.

Let ν be the applied frequency; $C_x=C_2-C_1$ the difference between the two readings of C_s; R the added resistance; C_v the vacuum capacity of test condenser. Then $R_x=R\ (C_2/C_x)^2$ is the equivalent series resistance of C_x; $f=2\pi\nu C_xR_x$ the power factor; and $\delta=C_x/C_v$ the dielectric constant.

Discussion of Results

Figs. 2 and 3 show the results obtained on castor oil and Hercules wood rosin "*F*." Because of the change of density, the normal behavior of the dielectric constant of a liquid is to decrease with increasing temperature. These curves, however, show a temperature region in which the dielectric constant increases. In the same region the power factor has a sharp maximum. The position of this region shifts with higher frequencies to higher temperatures.

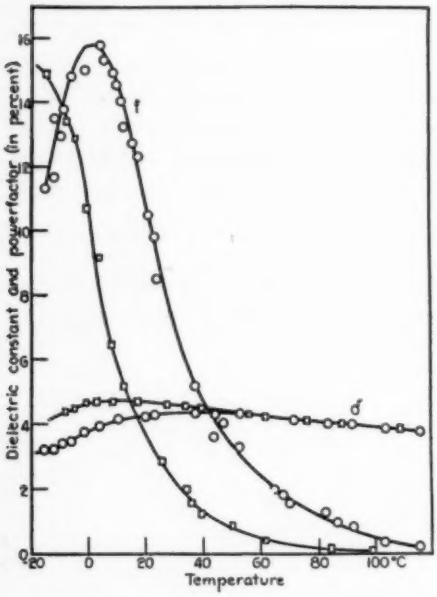

Fig. 2. Dielectric constant and power factor of castor oil as a function of temperature, at (□) 0.4×10^6 cycles, and (○) 10.9×10^6 cycles.

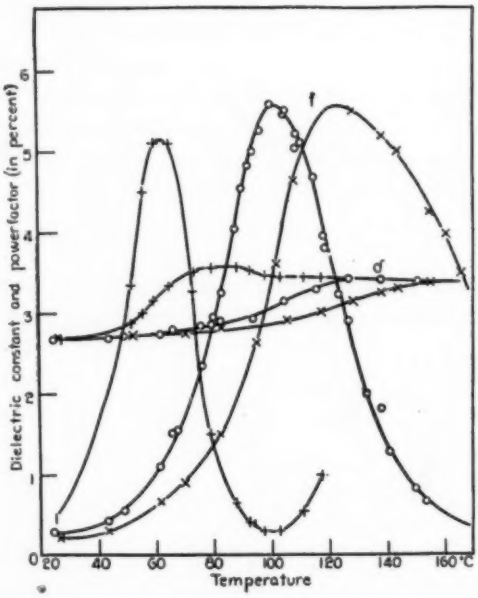

Fig. 3. Dielectric constant and pow e factor of wood rosin "*F*" as a function of temperature at (+) 60 cycles, (○) 10^6 cycles, (×) 10^7 cycles.

It is our opinion that this observed behavior cannot be explained on the basis of a heterogeneous dielectric as described, for example, in Maxwell's theory or its modification by K. W. Wagner,[1] Schweidler,[2] Pellat,[3] etc.

[1] K. W. Wagner, Ann. d. Physik **40**, 817, 833 (1913).
[2] Schweidler, Ann. d. Physik **24**, 742 (1907).
[3] Pellat, Ann. de chimie et phys. **18**, 150 (1899).

An explanation of these results, however, can be given on the basis of Debye's[4] theory of polar molecules, by assuming that the molecules of the main constituents of these liquids are electric dipoles. According to Debye's theory, one part of the dielectric polarization is due to the orientation of the polar molecules. This orientation has a relaxation time τ, which depends on the viscosity of the liquid. Considering the molecules as spheres of radius r turning in a viscous medium, Debye calculates the frequency $\nu_0 = 1/\tau$ corresponding to this relaxation time as

$$\nu_0 = kT/8\pi^2\eta r^3 \tag{1}$$

where $k = 1.37 \times 10^{-16}$ erg is Boltzmann's constant; T, the absolute temperature; η, the viscosity of the liquid; and r, the radius of the molecules.

The polar molecules cannot follow the changes in field for frequencies very much higher than ν_0. The polarization is then only due to the displacement of the electrons and the dielectric constant has therefore its optical value $\delta_\infty = n^2$. For frequencies very much smaller than ν_0, the relaxation can be neglected and the dielectric constant becomes independent of the frequency at its larger static value δ_0. In the neighborhood of ν_0, the dielectric constant decreases with increasing frequency, producing the so-called anomalous dispersion. In this region the relaxation produces a phase difference between the electric displacement (D) and the field strength (E). Therefore, the absorption coefficient α passes through a maximum in the region of anomalous dispersion.

Since the viscosity η usually decreases very much faster than $1/T$ with increasing temperature, the characteristic frequency ν_0 varies greatly with temperature. Representing, as we do, the dielectric constant at constant frequency as a function of the temperature, we must therefore find a temperature where the applied frequency coincides with ν_0. In the neighborhood of this temperature the dielectric constant increases, since the dipoles, which are fixed at low temperature, become liberated and, for the same reason as above, the coefficient of absorption or the power factor passes through a maximum. For a higher frequency the corresponding temperature must be higher, and hence the phenomenon shifts to higher temperatures with increasing frequencies.

So we see that Debye's theory explains, at least qualitatively, the observed behavior of the dielectric constant and power factor of rosin and castor oil. To prove rigorously that we are really dealing with the effect of anomalous dispersion, we should be able to check Debye's equation quantitatively.

We cannot, of course, expect to find Debye's equation accurately verified, but must be satisfied with results of the correct order of magnitude, for the following reasons: (1) Debye's equations hold exactly only for a gas in which all the molecules are dipoles. Rosin and castor oil, however, are viscous liquids and are furthermore not chemically uniform. (2) The coefficient of viscosity entering into Debye's formula is not necessarily identical with the

[4] P. Debye, Theorie der elektrischen und magnetischen Molekulareigenschaften, Marx's Handbuch der Radiologie **6**, 597–790. Leipzig, 1925.

macroscopically measured viscosity, and the quantity r is not the actual radius of the molecules but is only a length of the order of magnitude of molecular dimensions. (3) The formulas are applicable to experiments at constant temperature with variable frequency and, therefore, do not directly apply to our measurements. We shall nevertheless use these formulas. By doing so, we neglect the change of density of the liquid—i.e., we consider δ_0 and δ_∞ as independent of the temperature. Since their variations are small in the temperature region under consideration compared to the anomalous increase of δ, this cannot involve an appreciable error.

The position of the anomalous change of the dielectric constant at constant frequency is best characterized by the temperature for which the corresponding power factor is a maximum. This is not the temperature, however, at which the applied frequency coincides with ν_0 but the maximum occurs where

$$\nu=\nu_0\frac{\delta_\infty+2}{\delta_0+2}\left(\frac{\delta_0}{\delta_\infty}\right)^{1/2} \tag{2}$$

For rosin we have, approximately, $\delta_0=3.4$, $\delta_\infty=2.7$, therefore, $\nu=0.98\ \nu_0$. Since the measurements are subject to a possible error of 3 percent, we can neglect this difference for rosin. For castor oil, however, we have approximately $\delta_0=4.5$, $\delta_\infty=2.5$, therefore, $\nu=0.93\ \nu_0$, and the difference has to be taken into account.

If, in our experiments, we really are dealing with anomalous dispersion, we must show that equation (1) is satisfied, that is, that this equation leads to a reasonable value for r. Practically all the liquids which have hitherto been investigated show anomalous dispersion in the region of the spectrum between wave-lengths of 10 m and 0.1 cm.[5] Debye predicted, however, that liquids with large molecules and high viscosity should show the effect at lower frequencies. Castor-oil and rosin evidently satisfy both conditions. Fig. 4 represents our measurements of the viscosity curves of both liquids. These curves differ only slightly from the data given in Landolt-Börnstein. The departure is due to the difference in degree of refinement of the liquids.

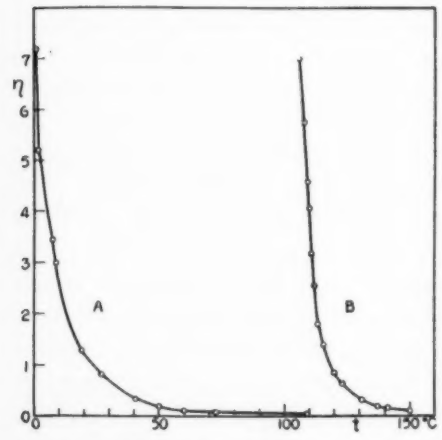

Fig. 4. Viscosity measurements for (A) castor oil and (B) rosin.

The maximum of the power factor of rosin for the frequency $\nu=10^7$ appears

[5] P. Drude, Zeits. f. Physik. Chemie **23**, 267 (1897). J. D. Tear, Phys. Rev. **21**, 611 (1923). Nichols and Tear, Phys. Rev. **21**, 587 (1923). S. Mizushima, Scientific Papers Inst. of Phys. Chem. Research **5**, No. 79. Tokyo 1927.

at the temperature $t=123°C$ ($T=396$). At this temperature, the viscosity is 0.63. Introducing these values in equation (1), we find a radius

$$r=(kT/8\pi^2\eta\nu)^{1/3}=4.8A$$

A molecular radius of rosin of this order of magnitude is certainly reasonable.

For castor oil, the maximum of the power factor for the frequency 10.9×10^6 is at $t=1°C$ ($T=274$), and the viscosity is about 7. By taking into account that $\nu=0.93\,\nu_0$, equation (1) leads to a radius $r=1.8A$.

The change of the characteristic temperature with frequency is also in good agreement with the theory. From (1) it follows that the temperatures T_1 and T_2, where the power factor for the frequencies ν_1 and ν_2 are maxima should satisfy the relation.

$$T_1\cdot\eta(T_2)/T_2\cdot\eta(T_1)=\nu_1/\nu_2 \tag{3}$$

For example in the case of rosin we have $T_1=396$ $\eta(T_1)=0.63$, $\nu_1=10^7$, $T_2=374$, $\nu_2=10^6$. The above relation is satisfied if we put $\eta(T_2)=6.7$. The extrapolation of the viscosity curve, on the other hand, gives a viscosity $\eta(374)$ of about 7.5. Since the temperatures are not very accurately determined, and since the viscosity changes so rapidly with temperature that a small variation of temperature produces a large change of the value of η the agreement must be considered satisfactory.

The shape of the curves dielectric constant and the power factor versus temperature is in accordance with the theory. We notice particularly that at lower temperatures the region of anomalous behavior is smaller. This can be explained by the rate of increase of viscosity with falling temperature. If the viscosity increased exponentially the regions would be of equal width. The viscosity curves however increase in slope more rapidly.

Debye's theory further predicts the magnitude of the maximum in the absorption coefficient.

$$\alpha\,(\max)=\frac{(\delta_0)^{1/2}-(\delta_\infty)^{1/2}}{(\delta_0)^{1/2}+(\delta_\infty)^{1/2}} \tag{4}$$

Power factor and absorption coefficient are related to each other according to the equation

$$f=2\alpha/(1-\alpha^2) \tag{5}$$

Hence the power factor maximum should have the value

$$f(\max)=(\delta_0-\delta_\infty)/2(\delta_0\delta_\infty)^{1/2} \tag{6}$$

Since δ_0 and δ_∞ do not vary much in the temperature region investigated, the maximum power factor should be independent of the frequency, as our results show.

$\delta_0-\delta_\infty$ is the part of the dielectric constant which is due to the orientation of the polar molecules. The larger this part is—i.e., the greater the number of polar molecules per unit volume or the larger the dipole moment of the single

molecules, the larger is the maximum power factor. A comparison of our results on rosin and castor oil verifies this conclusion. For rosin, $\delta_0 - \delta_\infty$ is about 0.7 and for castor oil about 2, while $(\delta_0\delta_\infty)^{1/2}$ has almost the same value. Accordingly, the maximum power factor of rosin is about one-third as great as that for castor oil. The polar molecules in castor oil evidently have a larger dipole moment than those in rosin.

The absolute value of the power factor is of the same order of magnitude as that calculated from equation (6) The observed value for rosin is about one-half the calculated one, namely 5.6 percent instead of 11.2 percent. Such deviations have to be expected in a substance containing different constituents.

A second series of experiments was carried out with solutions of rosin in different oils whose molecules were not polar. These solutions gave similar results—coincidence of maximum power loss and anomalous change of the dielectric constant both effects increasing in a parallel way with increasing concentration of the rosin. By changing the concentration of the solution or by changing the solvent the viscosity curve can be shifted and this offers a very convenient way to prove the importance of the viscosity for the position of anomalous dispersion.

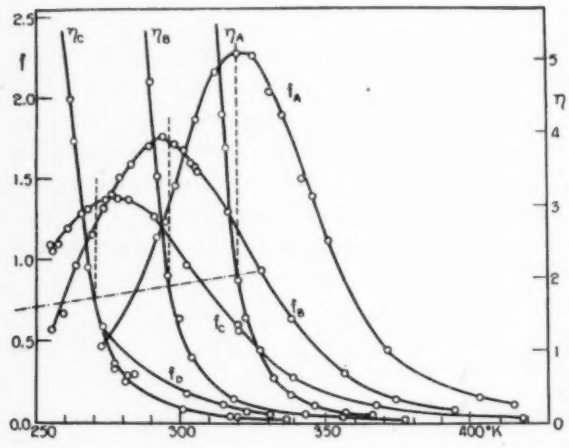

Fig. 5. Viscosity and power factor curves for mixture of rosin oil with transil oil at 10^8 cycles. (*A*) 100%, (*B*) 80%, (*C*) 50%, (*D*) 20% tosinoil.

Fig. 5 shows the viscosity curves and the power factor curves for one million cycles for three different mixtures of synthetic rosin oil with transil oil, and the power factor curve only for an additional mixture. Since v is constant, the maximum power loss should according to equation (1) occur at those temperatures where the ratio η/T assumes the same value. This fact is illustrated in the diagram. The "dot-dash" line coming from the absolute zero point, intersects the viscosity curves in points where the ratio η/T is the same. In agreement with the theory, the power factor maxima occur very close to the corresponding temperatures. These curves show very clearly the parallelism between viscosity and position of anomalous dispersion as demanded by Debye's theory.

In Fig. 3 we have also presented the curves power factor and dielectric constant of rosin versus temperature for a frequency of 60 cycles.[6] These

[6] For these curves, which were measured in the laboratories of the General Electric Co., we are indebted to the Hercules Powder Co.

curves are extremely interesting, because they show exactly the same features as the curves measured at radio frequencies We believe therefore that this is a case where anomalous dispersion appears at 60 cycles.

At 60°C where the maximum power loss appears rosin is semi-solid. It assumes the properties of an ordinary liquid only when heated above 100°, but there is no sudden change between these states. All its physical properties vary continuously in the whole temperature region as can be seen in our measurements of the dielectric constant. This indicates that rosin is still a liquid at room temperature but has a tremendous viscosity.

If we assume that Debye's equation (1) is still valid even for this highly viscous liquid, we have to ascribe to rosin at 60°C a viscosity of the order of magnitude of 10^5. R. Reiger[7] has calculated from observations of the elastic hysteresis of rosin that its viscosity should be of the order of magnitude of 10^{11}. Since Reiger may have used another kind of rosin and since the viscosity in this temperature region can easily be changed a few thousand times by small temperature variations or small additions of turpentine (which is a constituent of rosin) our value is compatible with Reiger's result. It is, of course, very doubtful that Debye's equation still holds for such very viscous substances, but any any rate it seems very probable that this is a true case of anomalous dispersion at 60 cycles.

In a third set of measurements we have been able to verify this result by means of optical investigations. Rosin and castor oil were two of the first materials in which Kerr[8] was able to observe electric double refraction Kerr found that in these two liquids the effect had a different character from that in all other substances. The problem has, however, never been investigated, since the experiments of Quincke made it doubtful, at that time, if in rosin the effect was not due merely to electrostriction and heating[9]. Debye's theory and our recent experiments explain the difficulties involved in these earlier experiments.

According to Langevin, Cotton-Mouton, and P. Debye[10] the Kerr effect is due to the orientation of the asymmetric molecules in the electric field. The effect can also exist in nonpolar substances but is especially strong in liquids with polar molecules In these substances the effect is mainly due to the orientation of the dipoles. Therefore, the Kerr effect has a relaxation time which is identical with the relaxation time of the electric polarization. This fact has been shown by the experiments of Blondlot[11] H. Abraham and Lemoine[12] J. James,[13] C. Gutton[14], etc. All these investigators measured the relaxation time after a sudden discharge of the Kerr cell and found values of

[7] R. Reiger, Phys. Zeits. **2**, 213 (1900).
[8] Kerr, Phil. Mag. **50**, 337, 446 (1875).
[9] W. Voigt in Graetz, Handbuch der Elektrizität und Magnetismus I.
[10] P. Debye, loc. cit. (4).
[11] R. Blondlot, Journal de phys. **7**, 91 (1888).
[12] H. Abraham and J. Lemoine, Journal de phys. **9**, 262 (1900).
[13] J. James, Ann. de Physique **15**, 954 (1904).
[14] C. Gutton, Journal de phys. **2**, 51 (1912); **3**, 266, 445 (1913).

τ of the order of 2×10^{-9} sec., corresponding to anomalous dispersion for waves of 60 cm wave-length or $\nu=5\times10^{8}$ as observed for ordinary liquids.

By producing the Kerr effect with an electric potential of this frequency, one should be able to observe an anomalous Kerr effect, namely a decrease of the Kerr constant with increasing frequency Since the observation of the Kerr effect requires potentials of at least a few thousand volts, such an investigation is impossible with ordinary liquids. The effect has only been discovered quite recently by C. V. Raman and S. C. Sirkar.[15]

The existence of anomalous dispersion in rosin for radio and audio frequencies makes it very easy to demonstrate this "anomalous Kerr effect," and the success of these experiments proves the existence of polar molecules in rosin.

A Kerr cell was filled with commercial white rosin, which is transparent in layers up to 10 cm thickness. The cell was 8 cm long, and the distance between the electrodes was 3 mm. The existence of the Kerr effect was observed in the usual way with help of two crossed nicols. Since rosin is optically active, it was necessary to use monochromatic light. This was obtained from a carbon arc with different light filters. By very slow cooling of the liquid rosin we were able to prevent internal stresses at lower temperatures. The voltage was measured with a spark gap parallel to the cell.

A d.c. voltage of 10 kv., furnished by electrostatic machine, produced at all temperatures an intense Kerr effect. Sixty cycle voltage, however, did not produce the slightest effect at room temperatures though the potential was increased to more than 75 kv. This certainly shows that the double refraction in this case cannot be due to electrostriction.

The effect of relaxation can easily be observed If the Kerr effect is produced with d.c and the voltage suddenly removed by closing the spark gap, the Kerr effect disappears gradually. At room temperature (20°C) the effect could still be clearly observed 30 seconds after the closing of the spark gap.

Using 60 cycle a.c. and raising the temperature of the rosin very slowly, the Kerr effect appears at 35°C first very faintly and increases gradually until it has the same intensity at 70°C as for the corresponding d.c voltage. The temperature at which the effect appears was fixed by leaving the rosin for 24 hours at constant temperature, once at 30° without obtaining any effect, and once at 35° with the first observable result.

These observations are in agreement with our measurements of the anomalous dispersion at 60 cycles. The curves in Fig. 3 show that the orientation of the polar molecules begins at about 35°C and reaches its full value at about 70°C.

We encountered many more difficulties in producing this anomalous Kerr effect with radio waves. For this purpose we built an oscillator, using a UX-852, 75 watt tube. The oscillator was coupled to a Tesla coil whose ends were connected to the electrodes of the Kerr cell. The frequency of the oscillator was adjusted to resonance with the circuit containing the Kerr con-

[15] C. V. Raman and S. C. Sirkar, Nature **121**, 794 (May 1928).

denser. The frequency was 1.5×10^6. According to our results in Fig. 3 the Kerr effect for this frequency should appear at about 100°C. At this temperature the rosin is liquid; since the anomalous dispersion is always connected with a maximum of absorption the high voltage used heats the substance. This heating effect produces a convection of the liquid which makes it almost impossible[16] to observe the Kerr effect. Since the disturbance due to convection requires about one second to appear, the effect can be seen for an instant after the field is applied.

After numerous trials we succeeded in this way in observing the Kerr effect for rosin at radio frequencies. The lowest temperature for which it was clearly seen was 115°. The effect may have existed at somewhat lower temperatures, but the difficulties of observation precluded any definite results.

Conclusions

The measurement of the dielectric constant and power factor and the observation of the Kerr effect show that castor oil and rosin are liquids with polar molecules. Because of the extremely high viscosity of these substances, the effect of anomalous dispersion and the anomalous change of the Kerr effect can be observed with radio frequencies and on rosin even at 60 cycles. These facts are important in three respects.

1. The existence of anomalous dispersion in the radio and audio region of the spectrum makes it possible to carry out accurate measurements of this effect and to test Debye's theory. Such an investigation is very desirable. We hope to be able to publish in the near future accurate data on chemically uniform materials. Our present measurements agree qualitatively with Debye's theory. The results of this investigation seem to point to the possibility of investigating the anomalous dispersion of practically any substance which may be dissolved in non-polar oils of proper viscosity.

2. The anomalous change of the Kerr effect with temperature and frequency represents a new effect to prove the theory of the orientation of the polar molecules.

3. The existence of anomalous dispersion in rosin at 60 cycles shows the importance of this effect in understanding the dielectric behavior of technical insulation materials. We believe that the curious behavior of many dielectrics as found by electrical engineers can be explained by the fact that polar molecules are present.

Chemical Research Laboratory,
Simplex Wire and Cable Co.
Cambridge, Mass.

[16] R. Leiser, Abhandlg. d. Bunsenges. No. 4, Halle 1910.

EFFECT OF DIFFRACTION AROUND THE MICROPHONE IN SOUND MEASUREMENTS

By Stuart Ballantine

Abstract

Proposed method of evaluating the pressure correction made necessary by diffraction.—The diffraction of sound around the diaphragm of the microphone ordinarily used in the measurement of the instantaneous pressure in a sound wave causes the indicated pressure to vary from equality with the actual pressure in the undisturbed wave at low frequencies, to twice this pressure at high frequencies. Because of the mathematically irregular shape of the conventional microphone and its mounting the effect cannot be calculated. It is proposed to evaluate the correction for diffraction by employing a standard spherical mounting of which the diaphragm occupies a small area about the pole; the increase in pressure for this mounting can be calculated theoretically, and the correction for other mountings can then be obtained by experimental comparison.

Theory of the diffraction of a sound wave by a rigid sphere.—The theory of the diffraction of a plane wave of the type $\exp i\omega(t-x/V)$ by a rigid sphere is outlined in terms of Hankel's $H^{2}_{n+\frac{1}{2}}$ functions, for which tables exist up to the highest orders required for the computations in practical cases. Numerical computations are carried out in full, giving the vector pressure ratio at the pole facing the source for spheres of various diameters and at various frequencies throughout the acoustic range.

IN MEASURING or recording instantaneous sound-pressure variations with a calibrated condenser microphone it is often assumed that the pressure at the diaphragm is the same as that which would exist in the undisturbed sound wave; also some investigators have assumed that the pressure is *doubled* by reflection, therefore that the apparent values are to be divided by a factor of 2. If the diaphragm were of infinite extent, or part of an infinite wall, the pressure would clearly be doubled at all frequencies since the reflection coefficient at the air-membrane interface is very closely equal to unity because of the stiffness of the tightly stretched membrane. If, on the other hand, the dimensions of the microphone were small in comparison with the wave-length of the sound, we should then have an ordinary problem of the Laplacian flow of air past an irregular obstacle and in these circumstances the pressure at the diaphragm would approach that in the undisturbed sound field. The effect of diffraction around the microphone then is to cause the apparent pressure (the pressure acting upon the diaphragm) to vary from the true pressure in the undisturbed wave, to twice this pressure as the frequency is raised from a low to a high value.

An obvious method of evaluating this effect and rendering useful the ordinary calibrations of the microphone derived from the application to the diaphragm of known alternating pressures produced by the thermophone, piston-phone or by electrostatic means, would consist in the direct comparison with the Rayleigh disk. The sound field at the point to be occupied by the microphone is first measured by means of the Rayleigh disk, the microphone

is then substituted and the overall calibration directly obtained in this way will include the effect of reflection. In the previous comparisons between the thermophone calibration of a condenser microphone and the Rayleigh disk calibration certain discrepencies have been noticed which are probably largely due to diffraction around the microphone.

The purpose of the present note is to consider the theory of the effect and to suggest a method for evaluating the appropriate corrections by means of a spherical mounting which can be calculated.

1. *Standard spherical mounting.* The geometrical volume occupied by the condenser transmitter and single-stage amplifier which is usually mounted with it for the purpose of avoiding long high-capacity leads, is of a mathematically irregular shape and not amenable to calculation To facilitate mathematical investigation we may mount the transmitter and amplifier in a substantially rigid spherical shell with the diaphragm as nearly in the surface as possible (Fig. 1). The diffraction of sound by a spherical obstacle is a classical problem[1] and tables now exist which greatly facilitate the actual numerical computations.

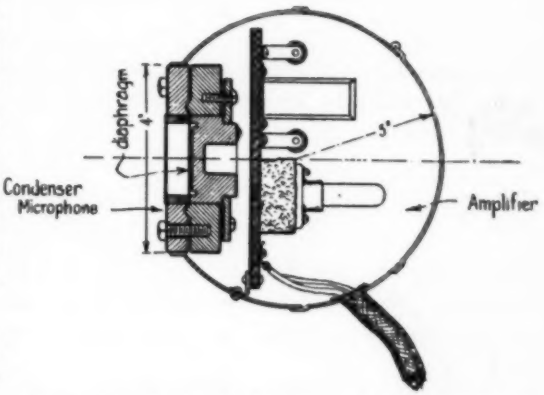

Fig. 1. Standard spherical mounting for condenser-microphone and amplifier stage.

When the relation between the pressure-ratio (actual pressure ÷ pressure in the wave in the absence of the obstacle) and frequency has been calculated for the standard spherical mounting the effect of diffraction with the more usual mountings may be readily evaluated by experimental comparison.

2. *Theory of diffraction of a plane sound wave by a rigid sphere.* With reference to a conventional spherical coordinate system with its polar axis along x we may imagine a plane sound wave of the form $e^{i\omega t}$ propagated from right to left in the direction of the polar axis; we require the pressure p at the pole facing the source or more accurately over a small circular area (representing the diaphragm) surrounding this pole. Since the problem has been discussed by the late Lord Rayleigh it will be sufficient here to indicate the form the solution takes when expressed in terms of Bessel functions whose order is half an odd integer, tables of which have become available since Rayleigh's treatment.

On account of the symmetry about the polar axis the wave-equation for the velocity-potential ϕ reduces to

[1] Rayleigh, "Theory of Sound," Vol. 2, p. 218 *et seq.* (London 1878): Papers, No. 287, vol. V, p. 112, 1903; No. 292, vol. V, 149, 1904.
Lamb, "Hydrodynamics," 5th Ed., p. 496 (Cambridge, 1924).

$$\frac{\partial^2\phi}{\partial r^2}+\frac{2}{r}\frac{\partial\phi}{\partial r}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\phi}{\partial\theta}\right)+k^2\phi=0, \tag{1}$$

where $k=\omega/V=2\pi\times$*frequency/velocity of sound in air.* The solutions of sufficient generality for our purpose are

$$\phi=\sum_{n=0}^{\infty}A_nP_n(\cos\theta)/r^{1/2}\begin{cases}J_{n+1/2}(kr)\\ J_{-n-1/2}(kr)\end{cases}; \tag{2}$$

where $P_n(\cos\theta)$ represents the Legendre polynomial of order n, θ being the polar angle (colatitude). We require the expression of exp $(i\omega x/V)$ in the form (2); this is given by Rayleigh's expansion:[2]

$$\phi_1=e^{ikx}=\sum_{n=0}^{\infty}i^n(2n+1)P_n(\cos\theta)(\pi/2kr)^{1/2}J_{n+1/2}(kr). \tag{3}$$

The scattering by the sphere can be most simply represented as a diverging spherical wave in terms of the second Hankelian Bessel functions of order $n+1/2$ thus

$$\phi_2=\sum_{n=0}^{\infty}A_nP_n(\cos\theta)(\pi/2kr)^{1/2}H^2{}_{n+1/2}(kr). \tag{4}$$

The complete solution is then: $\phi=\phi_1+\phi_2=$ Eq. (3)+Eq. (4). From the boundary condition at the surface of the sphere that the normal component of velocity ($\mathbf{v}=-$grad ϕ) shall vanish when $r=a$ or $\partial\phi/\partial r(r=a)=0$ we find

$$A_n=-i(2n+1)\frac{J_{n+1/2}(ka)-2kaJ'_{n+1/2}(ka)}{H^2{}_{n+1/2}(ka)-2kaH^{2\prime}{}_{n+1/2}(ka)}. \tag{5}$$

By taking advantage of the Wronskian relation

$$W(J_{n+1/2},J'_{n+1/2})=-(-)^n2/\pi x, \tag{6}$$

the solution represented by (3)+(4) reduces to the simple equivalent forms

$$\phi=\left(\frac{2}{\pi ka}\right)^{1/2}\sum_{n=0}^{\infty}\frac{-(2n+1)i^nP_n(\cos\theta)}{(-)^n(nJ_{-n-1/2}+kaJ_{-n-3/2})-i(nJ_{n+1/2}-kaJ_{n+3/2})}, \tag{7a}$$

$$=\left(\frac{2}{\pi ka}\right)^{1/2}\sum_{n=0}^{\infty}\frac{(2n+1)i^nP_n(\cos\theta)}{(-)^n[(n+1)J_{-n-1/2}+kaJ_{-n+1/2}]-i[(n+1)J_{n+1/2}-kaJ_{n-1/2}]}. \tag{7b}$$

The effect of diffraction may be most conveniently represented by the vector ratio of the pressure as calculated from (7) to that which would exist in the incident plane wave alone. Now the pressure $p=\rho\partial\phi/\partial t=i\omega\rho\phi$, where ρ is the air density, so that the ratio in question $p/p_0=$ eq. (7) $\div e^{ikx}$.

[2] Rayleigh, Proc. London Math. Soc. **4**, 253 (1873); H. M. MacDonald, "Electrical and Optical Wave Motion," p. 47 (Cambridge, 1900).

Since the diaphragm covers a finite (circular) area about the pole the variation of the pressure-ratio with θ should strictly be taken into consideration. Calculation indicates that for large values of ka the variation of the vector ratio is chiefly one of angle, the absolute value remaining substantially constant over a range of 15 degrees; for small ka the variation is chiefly in the amplitude. At $ka=0.3$ the variation of p/p_0 from $\theta=0$ to $\theta=15°$ is only about 1 percent. Moreover the pressure variation with θ must be "weighted," as the effectiveness of a pressure upon any annular element of the membrane falls off rapidly as the radius of the annulus approaches that of the membrane. It seems therefore that no serious error would be committed with a mounting of perhaps 6 in. diameter and a diaphragm of 1.5 in. diameter by regarding the polar pressure ($\theta=0$) as proportionate to the effective average pressure over the diaphragm at all frequencies.

3. *Computations and curves.* The pressure-ratio is a function only of the ratio of the size of the sphere to the wave-length of the sound. For computations from (7) tables are available[3] of $J_{n+1/2}$ for n up to 18, and of $J_{-n-1/2}$ for n up to 6; additional values of $J_{-n-1/2}$ for larger n may be computed from the tables of the related C_n functions given in the *British Association Reports* for 1914 (pp. 88–102) and 1916 (pp. 97–107). Computations made with the aid of these modern tables are given in Table I.

TABLE I. *Values of the vector ratio ($|p/p_0|e^{i\psi}$) of pressure at pole of rigid sphere to pressure in incident plane wave at same point for various values of $ka=2\pi\times$frequency$\times$radius of sphere $\div$velocity of sound in air.*

ka	$\frac{p}{p_0}$ Equation (7)	$\left\|\frac{p}{p_0}\right\|$	Angle ψ (radians)
0.1		1.0005	
0.2		1.0027	
0.3	0.909+0.458i	1.019	0.168
0.5	1.043+0.299i	*1.085	0.279
0.7	0.597+1.040i	1.198	0.345
0.85	0.468+0.374i	1.325	0.359
1.0	0.310+1.370i	1.406	0.340
2.0	1.593+0.468i	*1.660	0.286
3.0	−1.762−0.165i	1.772	0.235
4.0	−0.910−1.595i	1.835	0.194
6.0	1.895−0.292i	1.913	0.128
10.0	1.540+1.207i	*1.958	0.665 (?)

* Values calculated by the late Lord Rayleigh.[3]

The angle ψ of the vector ratio is given as well as the absolute value. This is of interest in estimating the dispersion which must be corrected by means of phase-equalizers in the electric circuits when an exact recording of the wave forms of the sound is desired. For many purposes, however, the absolute value alone will be sufficient.

Fig. 2 contains a set of curves based upon these computations which represent the effect of diffraction for spherical mountings of various sizes over the audio range of frequencies. The form of the correction curves for other

[3] G. N. Watson, "Bessel Functions," pp. 740–743 (Cambridge, 1922).

practical mountings may now be obtained experimentally by comparison with the standard mounting This experimental program is under way and will be reported in a subsequent paper. It is necessary to investigate the functional relation for a single size of each shape; the position of the curve for any other size may be determined by the principle of similitude.

In the case where the condenser transmitter is mounted integrally with the apparatus comprising the first amplifier stage and occupies a volume of reasonable (say cubical) shape it is often sufficient to estimate an "equivalent sphere" on the basis of equal volume to represent the irregular actual volume. The accuracy of this seemingly crude assumption is somewhat surprising.

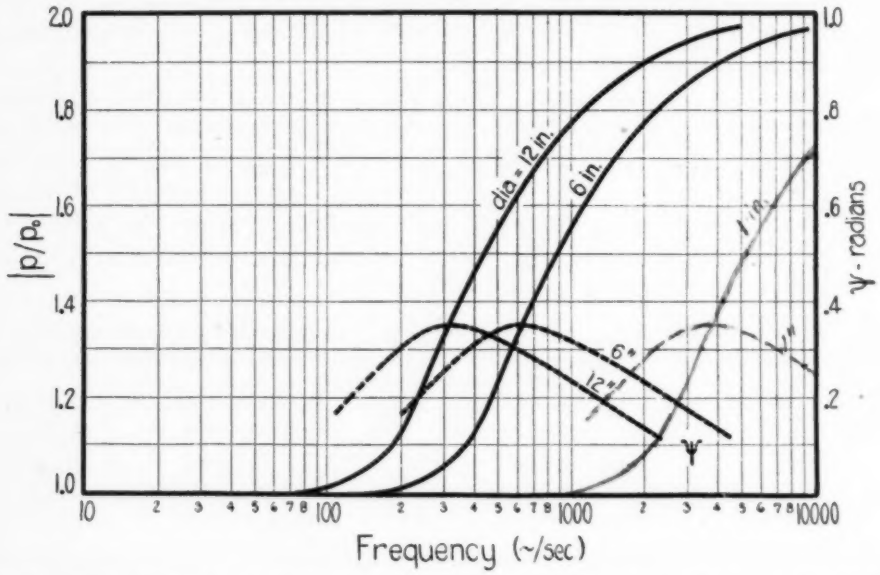

Fig. 2. Effect of diffraction of plane wave with spherical mountings: absolute value $|p/p_0|$ and angle ψ of ratio of pressure at pole of sphere to pressure in undisturbed wave.

Although the condenser microphone has been mentioned particularly in this discussion, it is obvious that it applies equally well to other pick-up instruments of the exposed diaphragm type, such as for example, the double carbon button microphone used extensively in radio broadcasting and public address systems. When the microphone is used for technical purposes and sound-wave recording it is convenient to compensate the diffraction effect either in the design of the microphone (which is feasible with air-damped types) or by equalization in the electrical circuits.

In conclusion it may be noted that by the reciprocity theorem equation (7) is equally appropriate for the representation of the pressure at a large distance in the sound radiated by a small piston located in the surface of a sphere. This throws some light on the action of baffles for loud-speakers.

RADIO FREQUENCY LABORATORIES, INC.,
BOONTON, N. J.
September 20, 1928.

ON THE ORIGIN OF THE AURORA POLARIS

By S. Chapman

Abstract

Hulburt's new theory of the aurora polaris is criticized on the ground, principally, that free high-atmospheric ions in middle and low latitudes cannot travel far towards the poles along the earth's lines of magnetic force, because they must at the same time descend into the lower levels where their motion is interrupted by collisions. Upward moving ions will travel towards the equator.

IN THE June issue of the Physical Review a new and interesting suggestion as to the origin of the aurora polaris is made by E. O Hulburt.[1] The theory generally current, due mainly to Birkeland and Störmer, is that the aurora is caused by the entry into the earth's amosphere of charged particles emitted from the sun, and directed towards the polar regions of the earth by the terrestrial magnetic field; in spite of many attractive features, this theory, when examined in detail, is found to offer some serious difficulties. The chief of these arises from the electrostatic repulsion which such charges exert on one another, tending to disperse the cloud of particles during their passage from the sun. There is consequently room for new auroral hypotheses which like that of Hulburt, do not involve this difficulty, if in other respects they are not less satisfactory than the current theory. The object of this note is to examine whether Hulburt's theory is really capable of explaining some of the principal facts about auroræ: the conclusion arrived at is adverse.

The new theory supposes that the aurora is due to the rapid diffusion of ions and electrons, produced by the sun's ultra-violet radiation at great heights in the atmosphere where the frequency of collisions is small, in neutral streams along the lines of magnetic force, resulting in a concentration of ions in the polar regions. There they move to lower levels and recombine, setting free their energy of recombination, which in some way causes the aurora. Thus the auroral energy comes from the sun in the form of ultra-violet radiation.

It is certainly true that at high levels there exist ions and electrons which between infrequent collisions, move almost freely subject only to gravity and the electromagnetic force due to the presence of the earth's magnetic field. The latter causes them to spiral round the lines of magnetic force, so that the average motion of the ions is in either direction along these lines. Except at the magnetic equator the lines are not horizontal. Assuming that the earth's magnetic field is that of a uniformly magnetized sphere (which is sufficiently exact for the present purpose) the equation of a line of force is

$$r/a = \cos^2\lambda/\cos^2\lambda_0,$$

[1] Hulburt, Phys. Rev. **31**, 1038 (1928).

where r is the radial distance from the earth's center, and λ the latitude, of a typical point on a line of force which passes through the point $r=a$, $\lambda=\lambda_0$. It is convenient to take a as corresponding to the level in the atmosphere where the mean free path is still short compared with the radius of the free spiral paths of the ions. The free ions are supposed to start from higher levels than this; they may move either upwards or downwards along a line of force in the inclined direction of the line. If they move upwards their horizontal motion is towards the equator, and they will travel in this direction, through layers of decreasing density, so far as is permitted by infrequent collisions and the retardation due to gravity. If they move downwards along the line of force they travel polewards, but they cannot go far in this direction before they reach the level $r=a$, where since they can no longer spiral freely, they become subject to ordinary gaseous conditions and have no appreciable tendency to move further along the lines of force.

Suppose that a particle starts at a height of 1000 km above the level $r=a$; in descending through this 1000 km along a line of force its horizontal poleward traverse will be largest if it starts above the equator, where the lines of force are horizontal. The latitude to which it will travel is obtained by putting $a=6000$ km $r=7000$ km, $\lambda=0°$ in the above equation (the value for a, given in round figures is rather too small, and will result in a somewhat too large value of λ_0); the result is approximately 22°. For a particle starting at the same level as this, but in latitude 30°, the poleward traverse is 6°. The value 22° can be regarded as an upper limit to the poleward traverse of an ion, since the level at which the ion-density must become insignificant for the purpose of this auroral theory is much less than 1000 km above the absorbing layer $r=a$. If the starting point is only 500 km above $r=a$ (and even this is excessive) the poleward traverse in the above two cases ($\lambda=0°$, $\lambda=30°$) is reduced to 16° and 4°; if $r-a=100$ km, $\lambda_0-\lambda=7°(\lambda=0)$, $1°(\lambda=30°)$. Thus except near the equator the ions cannot travel far towards the poles before they become absorbed in the denser layers beneath; and any ions diffusing upwards from these layers will, as they become free from collisions, travel equatorwards instead of polewards. There seems therefore to be no possibility of a stream of electrons passing from the middle belt of the earth into auroral latitudes. For an ion above the equator to travel freely even so far polewards as to latitude 60°, r must equal $4a$; at this height ($r-a=3a$ or 18000 km) there is no atmosphere. Hence the proposed theory seems incapable of explaining a polar concentration of ions produced in low latitudes by ultra-violet solar radiation.

Other objections against the theory may be stated.

(1) The aurora should, on the proposed theory be primarily a day-time phenomenon, its occurrence at night being simply a survival due to ions formed during the day, aurorae probably do occur invisibly during the day, but they are not seen most often just after sunset, but increase in intensity during the early hours of the night, while they have been seen to endure strongly until dawn.

(2) The theory seems incapable of accounting for the existence of the zone of maximum auroral frequency and for the thinness of auroral curtains, auroral features of which Störmer's theory offers an explanation.

(3) The earth's magnetic field does not increase the energy of the ions, and their power of penetrating the absorbing layer of the atmosphere will correspond merely to their velocity at their starting point. Aurorae appear to indicate the penetration of the atmosphere down to 90 or even at times, to 80 km which requires an amount of kinetic energy corresponding to some thousands of volts. Such energy is hardly likely to be acquired by many ions during the process of ionization by ultra-violet radiation.

(4) The tendency shown by marked outbursts of aurorae and magnetic disturbance to recur after the lapse of a solar rotation period is strong evidence for their production by means of a limited corpuscular stream from the sun, rather than by ultra-violet radiation. Such a stream might be regarded as the source of the ionization considered in Hulburt's theory without modifying the latter essentially: but the above arguments would still render it difficult to accept the theory of much poleward migration of ions formed in middle and low latitudes.

(5) It therefore seems necessary to suppose, as heretofore that aurorae are manifestations of the entry into the earth's atmosphere of solar corpuscles, which are deflected polewards, while still outside the earth's atmosphere, by the earth's magnetic field.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, ENGLAND.
June 4, 1928.

REPLY TO THE FOREGOING CRITICISM BY S. CHAPMAN

By E. O. Hulburt

Professor Chapman and the Editor have kindly permitted me to see the preceding paper by Professor Chapman. In reply I may say that the paper on the physics of the outer fringe of the earth's atmosphere has now been sketched out by Dr. H. B. Maris and me and will be offered for publication soon. We find that the ion spray caused by the ultra-violet light of the sun may reach heights of, say, 30,000 km above the equator. The prominent characteristics of the aurora apparently receive logical explanation. Quantitative estimates indicate that the ion spray may distil to within 20 to 30° from the magnetic poles (the zone of maximum auroral frequency) rapidly enough to supply the energy of the aurora. The estimates depend upon a knowledge of such quantities as the intensity of the solar ultra-violet light, Einstein's B, the fraction of excited atoms, etc. The quantities are imperfectly known but, as far as can be seen now, reasonable values are used.

Naval Research Laboratory,
Washington, D. C.
September 14, 1928.

ELECTRONIC STATES AND BAND SPECTRUM STRUCTURE IN DIATOMIC MOLECULES VII. $^2P \rightarrow {}^2S$ AND $^2S \rightarrow {}^2P$ TRANSITIONS. A CORRECTION.

By Robert S. Mulliken

In an article under the above title,[1] an unfortunate error occurs in the right hand side of the drawing (Fig. 3) showing energy levels and transitions corresponding to the OH bands. If correctly drawn, the figure would make the vertical lines representative of the ${}^{P}P_{12}$, Q_2, and ${}^{Q}R_{12}$ branches end always on A rotational sub-levels of the ${}^2P_{1/2}$ final state, while it would make the P_2, ${}^{P}Q_{12}$, Q_{2A2B}, and R_2 lines end always on B rotational sub-levels. The relative positions of A and B sub-levels in the figure are, however, correct as now shown.[2]

[1] R. S. Mulliken Phys. Rev. **32**, 406 (1928).

[2] The error in respect to the termini of the vertical lines arose from the fact that when the figure was first drawn, the A and B levels were (incorrectly) so labelled that every A level was above the corresponding B level.

BOOK REVIEWS

Atomstruktur und Atombindung. J. STARK. Pp. 218, figs. 15. Polytechnische Buchhandlung A. Seydel, Berlin, 1928. Price RM 6.

This book by the famous discoverer of the electric analogue of the Zeeman effect unites a set of conceptions usually considered incompatible. A static atom and valence theory is developed which purports to be in harmony with the equations of Maxwell's electrodynamics. The author accepts the corpuscular conception of light, the Rutherford nuclear picture of atomic structure, and the energy level hypothesis of Bohr. He assumes, however, that the electrons and protons have complicated electromagnetic fields with a concealed (and unspecified) cyclic motion of electromagnetic energy. Kinetic reactions or "inner-kinetic" forces due to this cyclic motion constitute a magic element which permits the electrons of an atom in a stationary state to remain in positions of static equilibrium under the influence of the ordinary electric attraction of the nucleus. The Bohr quantum conditions are replaced by frequency conditions applied to the inner-cyclic motions of electrons and protons. The exact nature of these conditions is unspecified.

The nucleus (except that of hydrogen) is assumed to be composed solely of units consisting of two protons and one electron. Neutral particles "vagabonding" between the nucleus and the K shell electrons are used to account for the existence of isotopes and to explain the failure of the approximate rule that the atomic weight of any element is twice its atomic number.

The reviewer finds the argument in general unconvincing.

E. C. KEMBLE

Photochemical Processes. GEORGE B. KISTIAKOWSKY. American Chemical Society Scientific Monograph No. 43, Pp. 270, Chemical Catalog Company, New York, 1928. Price $5.50.

Since the proposal of the Einstein Equivalence Law in 1912, there has been a steady acceleration of photochemical research. During this period of rapid expansion no one has ventured to collect, assort and evaluate the results, highly important though such an essay may have appeared. From all sides, therefore, a grateful welcome should meet the present monograph by Dr. Kistiakowsky, which he modestly entitles "Photochemical Processes."

The subject is naturally approached from the stand-point of light quanta as proposed by Einstein. In a brief but authoritative foreword, Professor H. S. Taylor emphasizes a fact frequently overlooked that while the quantum controls the primary photochemical action, the photochemical yield is determined by succeeding thermal reactions merely initiated by the light absorption. As additional guiding principles Kistiakowsky employs the modern concepts of spectroscopy as represented by line, band and continuous spectra and the energy changes and atomic states, associated with them. These are subjects in which physicists and photochemists share an equal interest and which are sure to have an increasing importance as they are more fully mastered.

The processes dealt with are chain reactions, photosensitization, catalysis and inhibition, and the frequency of radiation and temperature as influencing the rate of reaction.

Instead of dealing abstractly with processes and principles, the writer has wisely chosen to consider them by means of the most representative experimental data assembled for typical photochemical reactions. This method not only lends the necessary flexibility to the treatment of photochemistry in its present state of development, but gives the student and research worker an invaluable index to the principal work on each reaction dealt with. The author has adequately supplied the essential connections of principle to link up the different reactions with as much continuity as is possible at present. In doing this he has shown an admirable grasp of the material at hand.

The author has not failed to carry out one of the main objects of the monograph series "by pointing out directions in which investigations needs to be extended." There are many such directions to which the present work not only forms a stimulating guide but an indispensible store of information and correlation of what has already been accomplished.

S. C. LIND

Das Periodische System in neuer Anordnung, mit Tabellen über fünfzehn physikalische Constanten in Anordnung nach der Ordnungszahl der Elemente und nach der Grösse der Constanten. DR. DARWIN O. LYON. Pp. 40. Franz Deuticke, Leipzig and Wien, 1928. Price RM 10.

The somewhat formidable title of this pamphlet constitutes almost a review in itself, and my task is correspondingly lightened. The author has interested himself in the problem of the distribution of the 92 chemical elements throughout the universe, and in order to understand this problem better has collected and arranged in various suggestive ways the best available values of a number of the physical properties of the elements. Doubtless the most important single feature is Table IV, in which the elements are arranged in 15 different orders according to the numerical values (which are given) of the following 15 physical properties: atomic number, atomic weight, density of the solid, density of the liquid, thermal expansion of the solid, thermal expansion of the liquid, melting point, boiling point, latent heat of melting, latent heat of vaporization, specific heat, electrical resistance, magnetic susceptibility, entropy, and velocity of sound. There is considerable discussion of the correlations between these different properties. Other suggestive arrangements of the material are offered, among which the three arrangements of the elements in three different spiral orders are interesting. Charts are given of the numerical values, which usefully emphasize relative values, and exhibit the places where data are missing.

The value of this collection has been fairly enough indicated by the author himself on page 37: "A comparison of the data contained in the different columns lays before the eye the regularities and the exceptional features in the behavior of the constants, and stimulates to speculative considerations. Whatever value one may ascribe to the relations thus brought to light, they certainly are of interest, and may even in many cases lead the way to new knowledge."

P. W. BRIDGMAN

An Account of the Principles of Measurement and Calculation. NORMAN ROBERT CAMPBELL. Pp. 293. Longmans Green and Company, New York, 1928. Price $5.00.

This is a serious and important attempt to formulate the logical principles which more or less unconsciously guide every physicist in his attempt to describe the world about him in terms of measurement. The author claims, and as far as I know his claim is entirely justified, that this is the first book of its kind; it is not easy to understand why something of the kind has not been attempted before. The book is written in the trenchant style which we have come to expect of Campbell; this adds much to the readability, but sometimes has the disadvantage that "certain parts of the book have an undesirable air of controversy," as the author himself recognizes in the preface.

Many parts of the book will no doubt not command common assent, but this need not detract from its usefulness. Personally, I am not in sympathy with the fundamental point of view, which is that there are in nature things which may be defined with the complete logical precision which we have come to associate with the entities of the mathematician. Campbell's discussion of weighing brings out the point at issue. The masses of two bodies are defined with respect to their behavior in a balance; that one of two bodies is defined as being the heavier which sinks when balanced against the other. Of course it is recognized that every balance has a certain insensitivity, such that two bodies may be indistinguishable from each other. But it is also true that although B may be indistinguishable from A and C indistinguishable from B, nevertheless A may be distinguishable from C. This gives a means of finding whether A is heavier or lighter than B, although it may be indistinguishable from it. For evidently A

is lighter than B if it is possible to find any third body C such that A is lighter than C while B is indistinguishable from C. By a continued application of this process, which in practise may be impossibly tedious, but which is nevertheless possible in principle, Campbell proposes to arrange all masses in an ordered series, characterized by the relations $>, =, <$. This means that mass is a "magnitude," magnitude having a logically precise definition, which is irrelevant for our immediate purpose. The unsuspecting reader will doubtless be a little awed at the necromancy which has succeeded in investing with such logical precision the sinful testimony of our senses, but I believe that we can discover the *deus ex machina* in the assumption made about the balance. It is assumed that when weights are placed in the pans either one pan will go down or it will not. But no balance behaves in this categorical way when pushed to the limit, but ultimately refuses to say either yes or no to our questions, the pointer taking refuge in the vascillations of the Brownian movement.

I feel much more confidence now in urging the essentially unprecise quality of every physical quantity than I would before the formulation of the Heisenberg principle of uncertainty. The following quotation, which seems fairly characteristic of Campbell's general attitude, now hardly calls for comment in view of this principle. "Furthermore, the theory states that E_m (minimum error) is determined by the instrument used for judging 'the relation of indistinguishability'* rather than by the system judged." (p. 138). We would now say that measuring instrument and system form an undissociable whole, and that it is not possible to associate the irreducible errors of measurement with either part of the whole.

Although we cannot, for these reasons, admit that Campbell has been successful in his logical analysis, we can nevertheless, I believe, recognize that some such program as that of Campbell is one which we may asymptotically approach as the scale of phenomena becomes larger, and recognize a corresponding practical value in his exposition.

P. W. BRIDGMAN

* My rendering for one of Campbell's formal symbols.

AUTHOR INDEX TO VOLUME 32

References with (A) are merely to abstracts of papers presented at meetings of the Physical Society.

Allison, Samuel K. An experimental study of the relative intensities of x-ray lines in the *L*-spectrum or uranium—1

Anderson, Wm. T. Jr. and **Lester F. Bird.** The measurement of ultra-violet quanta by fluorescence photometry—293

Babcock, Harold D. A preliminary examination of Langley's bolometric data on the solar spectrum—326(A)

——— and **W. P. Hoge.** An extension to the photographic study of the infra-red solar spectrum—327(A)

Ballantine, Stuart. Effect of diffraction around the microphone in sound measurements—988

Barnes, James and **W. H. Fulweiler.** The absorption spectrum of liquid benzene—618

Barrett, Charles S. The scattering of x-rays from gases—22

Beams, J. W. (see Lawrence, Ernest O.)—478

Beattie, James A. The entropy and thermodynamic potentials of real gases and mixtures of real gases and a mass action law for chemical reaction between real gases: II. Integrated equations—691

——— The entropy and thermodynamic potentials of real gases and mixtures of real gases and a mass action law for chemical reaction between real gases: III. Relations for pure gases, and the equilibrium pressure of a gas in a mixture—699

Bennett, R. D. (see Lauritsen, C. C.)—322(A), 850

Bennett, Willard H. and **Charles F. Meyer.** The infra-red absorption spectra of the methyl halides—888

Bichowsky, F. Russell. A generalized Gibbs-Boltzmann equation—494

Bidwell, C. C. A simple relation between thermal conductivity, specific heat and absolute temperature—311

Bird, Lester F. (see Anderson, Wm. T. Jr.)—293

Bourgin, D. G. An approximation method and application to some HCl bands—237

Boyce, J. C. (see Compton, K. T.)—179

Bozorth, Richard M. Time-lag in magnetization—124

Breit, G. Book Reviews—150, 315, 706

——— The propagation of Schroedinger waves in a uniform field of force—273

——— The principle of uncertainty in Weyl's system—570

Brickwedde, F. G. (see Wait, G. R.)—967

Bridgman, P. W. Book Reviews—317, 999,

Brown, Hugh M. Effect of magnetic fields upon thermal conductivity of Fe, Cu, Au, Ag and Zn—508

Bryan, A. B. and **I. C. Sanders.** The dielectric constant of air at radio frequencies—302

Burt, Robert C. An erythema meter—320(A)

——— An ultra-violet photometer—326(A)

Cameron, G. H. (see Millikan, R. A.)—533

Canfield, R. H. Internal friction in metals—520

Cassen, Benedict. On the concentration of space charge in the vicinity of an insulating surface—323(A)

——— On measurable functions of dynamical variables—326(A)

Chapman, S. On the origin of the aurora polaris—993

Claus, W. D. (see Jauncey, G. E. M.)—12

Cohen, Lillian. Book Review—532

Cohn, B. E. (see Nyswander, R. E.)—321(A)

Collins, E. Hobart. The fine structure of the sharp series triplet, $2^3P_{0,1,2}-2^3S_1$, of optically excited Hg radiation—753

Compton, K. T. Book Review—840

——— **J. C. Boyce** and **H. N. Russell.** Extreme ultra-violet spectrum of argon excited by controlled electron impacts—179

Condon, Edward U. Nuclear motions associated with electron transitions in diatomic molecules—858

Constant, F. Woodbridge. The distribution of the heat emission in the magnetic hysteresis cycle—486

Cornog, I. Clyde. A study of the energy relations in the helium spectrum—746

Coulliette, J. Horace. The diffusion of metastable atoms in Hg vapor—636

Davis, Bergen and **Dana P. Mitchell.** Fine structure of the scattered radiation from graphite—331

——— and **Harris Purks.** Note on the effect of chemical combination on the structure of the *K* absorption limit—336

Dewey, Jane M. Spectral excitation by recombination in the electric arc—918

Dodd, L. E. Locus of secondary image for two plane mirrors independently variable about parallel axes situated in the two respective planes—320(A)

DuBridge, Lee A. The thermionic and photoelectric emission from Pt and Pd—325(A)

——— The thermionic emission from clean Pt—961

Edwards, Hiram W. Total reflection of x-rays from Ni films of various thicknesses—712
Ellis, Joseph W. Heats of linkage of C-H bonds from vibration spectra—324(A)
——— Visible absorption bands of colorless liquids and their relation to infra-red bands—906
Epstein, Paul S. Interference of reflected light—328(A)
Erikson, Henry A. The effect of water vapor on the mobility of gaseous ions in air—791

Ferguson, Donald. Book Review – 151
Ferguson, W. F. C. The less refrangible bands in the spectrum of tin monochloride—607
Fry, Thornton C. and **Herbert E. Ives.** The voltage-current relation in central cathode photoelectric cells—44
Fulweiler, W. H. (see Barnes, James)—618

Ganesan, A. S. The spark spectrum of neon—580
Gartlein, C. W. The first spark spectrum of arsenic, As II—320(A)
Gibbs, R. C. (see Vieweg, Alice M.)—320(A)
——— and **H. E. White.** Doublets and quartets of doubly ionized silver, Ag III—318(A)
Goetz, A. Single crystals of metals formed in magnetic fields—322(A)
Gunn, Ross. The diamagnetic layer of the earth's atmosphere and its relation to the diurnal variation of terrestrial magnetism—133
Gurney, Ronald W. Scattering of positive ions from a Pt surface—467
——— Efficiency of ionization in hydrogen by positive-ion impact at 7000 volts—795

Hales, Wayne B. Critical photoelectric potential of clean Hg and the influence of gases and of the circulation of the Hg upon it—950
Hall, E. L. (see Wait, G. R.)—967
Hamilton, Hugh. Measurement of arc voltage across opening switch contacts—322(A)
Hansen, Wm. W. (see Pearson, Gerald L.)—325(A)
Harkness, R. W. (see Hogness, T. R.)—784, 936
Hicks, Hervey C. Lagrangian functions which determine a symmetrical tensor by Schroedinger's rule—322(A)
Hill, E. and **J. H. VanVleck.** On the quantum mechanics of the rotational distortion of multiplets in molecular spectra—250
Hodges, A. C. Effect of pressure and current density on the spectrum of helium—319(A)
Hodges, Clarence and **W. C. Michels.** Intensity measurements in the helium spectrum—913
Hoge, W. P. (see Babcock, Harold D.)—327(A)
Hogness, T. R. and **R. W. Harkness.** The ionization processes of iodine interpreted by the mass spectrograph—784
——— and **R. W. Harkness.** The ionization of carbon monoxide by controlled electron impact, interpreted by the mass spectrograph—936
——— and **H. W. Kvalnes.** The ionization processes in methane interpreted by the mass spectrograph—942
Hoyt, Frank C. Polarization of the resonance radiation from degenerate systems—377
Hulburt, E. O. The intensities of the lines in the spectrum of Hg—593
——— On the origin of the aurora polaris. A reply to a criticism—996
Humphreys, C. J. (see Sawyer, R. A.)—583
Hyatt, J. M. Secondary electron emission produced by positive caesium ions—922
——— and **H. A. Smith.** Secondary electron emission from molybdenum—929

Ingersoll, L. R. and **L. O. Sordahl.** Temperature of the cathode as a factor in the sputtering process—649
Ingram, S, B. The spectrum of sulphur, S II—172, 318(A)
Ives, Herbert E. (see Fry, Thornton C.)—44
——— **A. R. Olpin** and **A. L. Johnsrud.** The distribution in direction of photoelectrons from alkali metal surfaces—57

Jauncey, G. E. M. and **W. D. Claus.** Interpretation of atomic structure factor curves in crystal reflection of x-rays—12
Johnson, J. B. Thermal agitation of electricity in conductors—97
Johnsrud, A. L. (see Ives, Herbert E.)—57
Jones, R. N. Anomalous magnetic rotation in excited neon—681
Jones, T. J. Absorption coefficient of slow electrons in Hg vapor—459

Kemble, E. C. Book Review—998
Kenty, Carl. The recombination of argon ions and electrons—624
——— and **Louis A. Turner.** Surface layers on tungsten and the activation of nitrogen by electron impact—799
King, Arthur S. Structure of praseodymium lines—319(A)
Kistiakowsky, G. B. Book Review—150
Kitchin, Donald W. and **Hans Müller.** Anomalous dispersion, absorption and Kerr effect in viscous dielectrics—979

Knauss, Harold P. Band spectra in the extreme ultra-violet excited by active nitrogen—417
Knudsen, Vern O. The insulation of vibration—324(A)
Korff, Serge A. (see Stewart, John Q.)—676
Kvalnes, H. W. (see Hogness, T. R.)—942

Lang, R. J. On the spectra of doubly ionized arsenic antimony and bismuth—737
Lark-Horovitz, Karl and **George W. Sherman.** Photoelectric control with mirror reading instruments—328(A)
Lauritsen, C. C. and **R. D. Bennett.** A new high voltage x-ray tube—322(A), 850
——— **and S. S. Mackeown.** Electric fields near the surface of tungsten wire of small diameter—326(A)
Lawrence, Ernest O. and **J. W. Beams.** The element of time in the photoelectric effect—478
Lee, F. W. Book Review—151
Lind, S. C. Book Review—998
Lindsay, R. B, High frequency sound radiation from a diaphragm—515
Lindvall, F. C. Gas phenomena and contact behavior in a vacuum switch—321(A)
Loeb, Leonard B. Recent light on the nature of gaseous ions—81
Loomis, F. W. and **S. W. Nile, Jr.** New features of the red band system of Na—873
——— and **R. W. Wood.** The rotational structure of the blue-green bands of Na_2—223

Mackeown, S. S. (see Lauritsen, C. C.)—326 (A)
Magie, W. F. Book Review—317
Maxwell, L. R. The determination of the mean life for the 4797A spark line of doubly ionized Hg—721
——— The spectra of Hg above the ionization potential—715
McKeehan, L. W. Book Reviews—531
Meyer, Charles F. (see Bennett, Willard H.)—888
Michels, W. C. (see Hodges, Clarence)—913
Miles, J. B., Jr. (see Zahn, C. T.)—497
Miller, K. J. Note on magnetic properties of evaporated films of Ni—689
Millikan, Clark B. Some problems in the steady motion of viscous, incompressible fluids; with particular reference to a variation principle—323 (A)
Millikan R. A. and **G. H. Cameron.** The origin of the cosmic rays—533
Mitchell, Dana P. (see Davis, Bergen)—331
Morris, J. C., Jr. Comparison of measurements of critical potentials of Hg vapor—447
——— Ionizing potentials of methane, ethane, ethylene, and acetylene—456
Mott-Smith, L. M, The absence of effect of an electric field on the magnetic susceptibilities of HCl and NO—817
Müller, Hans. (see Kitchin, Donald W.)—979
Mulliken, Robert S. The assignment of quantum numbers for electrons in molecules I—186
——— The assingment of quantum numbers for electrons in molecules. II. Correlation of molecular and atomic electron states—761
——— Electronic states and band spectrum structure in diatomic molecules. VII. $^1P \rightarrow {}^1S$ and $^1S \rightarrow {}^1P$ transitions—388; Correction—997
——— Interpretation of the atmospheric absorption bands of oxygen—880
——— (see Van Vleck, J. H.)—327(A)

Nielsen, Harold H. The near infra-red vibration spectrum of the carbonates—773
Nile, S. W., Jr. (see Loomis, F. W.)—873
Nyquist, H. Thermal agitation of electric charge in conductors—110
Nyswander, R. E. and **B. E. Cohn.** Measurements of thermo-luminescence of glass exposed to light—321(A)

O'Brian, Brian and **E. Dickerman O'Brien.** Instantaneous line intensities in the alternating current arc—321(A)
O'Day, Marcus. The function of a horn in acoustics—328(A)
Olpin, A. R. (see Ives, Herbert E.)—57
Olson, Harry F. Polarization of resonance radiation in Hg—443
Oppenheimer, J. R. On the quantum theory of electronic impacts—361

Page, Leigh. Book Review—706
Pardue, L. A. and **J. S. Webb.** Ionic oscillations in the glow discharge—946
Pearson, Gerald L. and **Wm. W. Hansen.** Superposition of x-rays—325(A)
Pfund, A. H. Metallic reflection from rock-salt and sylvite in the far ultra-violet—39
Phillips, Marcella Lindeman. Visible radiation characteristics of incandescent oxides—832
Pietenpol, C. J. The direction of ejection of photoelectrons by polarized x-rays—564
Podolsky, Boris. Quantum-mechanically correct form of Hamiltonian function for conservative systems—812
Pugh, Emerson M. Hall effect and magnetic induction in a bar of electrolytic iron—321 (A), 824
Purks, Harris. (see Davis, Bergen)—336

Rainich, G. Y. Book Review—316
Rice, Oscar Knefler. The energy distribution of complex molecules—142

Rojansky, V. and **J. H. VanVleck.** The non-metastability of the 2*s* level in atomic hydrogen—327(A)
Roller, Duane. Effect of toluene on the photoelectric behavior of Hg—323(A)
Ruedy, Richard. On free and bound electrons in metals—974
Rusk, Rogers D. The combination of hydrogen and oxygen by electric discharges—287
Russell, H. N. (see Compton, K. T.)—179
Russell, H. W. The potential of photoactive cells containing fluorescent electrolytes—667

Sanders, I. C. (see Bryan, A. B.)—302
Sanford, Fernando, An experimental method of measuring the electrostatic induction of the sun's negative charge upon the earth—325(A)
Sawyer, R. A. and **C. J. Humphreys.** The 29 and 30-electron-system spectra of arsenic and selenium—583
Schwarzschild, M. M. Theory of the double x-ray spectrometer—162
Shenstone, A. G. The first spark spectrum of palladium (Pd II)—30
Sherman, George W. (see Lark-Horovitz, Karl)—328(A)
Slater, J. C. The self consistent field and the structure of atoms—339
——— The normal state of helium—349
Smith, H. A. (see Hyatt, J. M.)—929
Smith, Sinclair. An optical oscillograph—319(A)
Smyth, H. D. and **E. C. G. Stueckelberg.** Ionization by collisions of the second kind in mixtures of oxygen with the rare gases—779
Sordahl, L. O. (see Ingersoll, L. R.)—649
Stebbins, Joel. Book Review—532
Stern, T. E. On the precise determination of thermal capacities with particular reference to that of molybdenum—298
Stewart, G. W. X-ray diffraction in liquids: a comparison of isomers of normal heptane and of certain carbon chains—153
——— Theory of x-ray diffraction in liquids—558
Stewart, John Q. and **Serge A. Korff.** The refractive index of Na vapor and the width of the *D* lines in absorption—676
Strout, Roger S. The temperature coefficient of quartz crystal oscillators—829
Stueckelberg, E. C. G. (see Smyth, H. D.)—779

Tonks, Lewi. Note on thermionic emission—284
Turner, Louis A. Ionizing potentials and far ultraviolet lines of light atoms—727
——— (see Kenty, Carl)—799

Ufford, C. W. The electrical resistance of alloys under pressure—505

Van den Akker, J. A. and **E. C. Watson.** The direction of ejection of x-ray electrons—323(A)
VanVleck, J. H. (see Hill, E.)—250
——— (see Rojansky, V.)—327(A)
——— and **Robert S. Mulliken,** On the widths of σ-type doublets in molecular spectra—327(A)
Vieweg, Alice M. and **R. C. Gibbs.** An extension of the Cd I-like iso-electronic sequence to Sb IV—320(A)

Wadlund, A. P. R. Absolute x-ray wave-length measurements—841
Wahlin, H. B. The critical potentials of metallic vapors: I. copper—277
Wait, G. R., F. G. Brickwedde, and **E. L. Hall.** Electrical resistance and magnetic permeability of iron wire at radio frequencies—967
Waring, R. K. Absorption bands in the spectra of mixtures of metallic vapors—435
Warner, A. H. The variation of the photoelectric effect with temperature, and a determination of the long wave-length limit for tungsten—326(A)
Watson, E. C. (see Van den Akker, J. A.)—323(A)
Watson, William W, Beryllium hydride band spectra—600
Weatherby, B. B. A determination of the wave-length of the $K\alpha$ line of carbon—707
Webb, J. S. (see Pardue, L. A.)—946
Webster, David L. and **Robert M. Yeatman.** Recombination of ions in the chamber of an x-ray spectrometer—325(A)
Welch, George B. Photoelectric thresholds and fatigue—657
Welo, Lars A. On negative values of θ in the law of paramagnetism $K(T-\theta)=C$—320(A)
White, H. E. On the spectra of doubly ionized vanadium, V III, and triply ionized chromium, Cr IV—318(A)
——— (see Gibbs, R. C.)—318(A)
Wilson, Earl D. Absorption band spectrum of iodine monochloride—611
Winans, J. G. The fluorescence and absorption of a mixture of Hg and Zn vapors—427
Wood, R. W. (see Loomis, F. W.)—223

Yeatman, Robert M. (see Webster, David L.)—327(A)
Yensen, T. D. Evidence obtained by x-ray analysis of films of iron in magnetic fields as to the ultimate nature of magnetism—114

Zahn, C. T. and **J. B. Miles, Jr.** The dielectric constant and the electric moment of CO, COS, CS_2, and H_2S—497
Zwicky, F. On the thermodynamical equilibrium of the universe—324(A)

ANALYTIC SUBJECT INDEX TO VOLUME 32

References with (A) are merely to abstracts of papers presented at meetings of the Physical Society.

Absorption of light (see also Spectra, X-rays)
By carbonates, infra-red, theory, Harold H. Nielsen—773
By liquid benzene, infra-red, wave-lengths, J. Barnes, W. H. Fulweiler—618
By methyl halides, infra-red, W. H. Bennett, C. F. Meyer—888
By mixtures of Hg and Zn vapors, J. G. Winans —427
By Hg, Tl and by In, Cd vapors, bands, R. K. Waring—435
By organic liquids, heats of linkage of C-H bonds, J. W. Ellis—324(A)
By organic liquids in visible region, relation to infra-red bands, J. W. Ellis—906
By Na vapor, width of *D* lines, relation to refractivity, J. Q. Stewart, S. A. Korff—676

Acoustics
Effect of diffraction around microphone, S. Ballantine—988
Function of horns, M. O'Day—328(A)
High frequency sound radiation from diaphragm, R. B. Lindsay—515

Activated gases
Activation of N_2 by electron impact, C. Kenty, L. A. Turner—799
Active nitrogen, excitation of band spectra in CO and NO, mechanism, H. P. Knauss—417
Hg^{++}, mean life for λ 4797 line, L. R. Maxwell —721
Ne, dispersion constants and magnetic rotation, R. N. Jones—681

Adsorption
Of active nitrogen on tungsten, C. Kenty, L. A. Turner—799

Afterglow
In argon, recombination spectra, C. Kenty—624

Alloys
Li-Sn, Bi-Sn, Ca-Pb, Ca-Mg, electrical resistance under pressure, C. W. Ufford—505

Approximation method
Application to HCl band intensities, D. G. Bourgin—237

Arcs (see also Discharge of electricity in gases)
Measurement of arc voltage, H. Hamilton—322 (A)
In He, ion concentration and recombination spectra, J. M. Dewey—918
In H_2, O_2 mixtures, rate of chemical reaction, R. D. Rusk—287

Atom-building
Energy released in process, kinetics of, relation to cosmic rays, R. A. Millikan, G. H. Cameron —533

Atomic structure (see also Energy states; Mechanics, quantum; Spectra)
Application of method of self consistent fields, J. C. Slater—339
Of He, normal state, theory, J. C. Slater—349

Aurora
Criticism of Hulburt's theory of origin, S. Chapman—993
Reply to Chapman, E. O. Hulburt—996

Avogadro's number
Calculation based on x-ray measurement, A. P. R. Wadlund—841

Book Reviews
Abegg, R., Fr. Auerbach and I. Koppel, Handbuch der Anorganischen Chemie. Volume Four, Section Three, Part One, The Rare Gases. Eugen Rabinowitsch—532
Campbell, Norman Robert, An Account of the Principles of Measurement and Calculation —999
Chazy, Jean, La Théorie de la Relativité et la Méchanique Céleste—706
Dingler, Hugo, Das Experiment, Sein Wesen und Seine Geschichte—317
Eichenwald, A., Vorlesungen über Elektrizität —315
Frenkel, J., Lehrbuch der Elektrodynamik. Band II, Makroskopische Elektrodynamik der Materiellen Körper—315
Gerlach, Walter, Matter, Electricity, Energy— 150
Graetz, L., Handbuch der Elektrizität und des Magnetismus. Band V, Lieferung 2—151

Book Reviews—cont.
Graetz, L., Handbuch der Elektrizität und des Magnetismus. Band V, Lieferung 3—706
Joffè, Abram F., The Physics of Crystals—531
Kistiakowsky, George B., Photochemical Processes—998
Laures, Clement, Les Bases de La Geometrie et de la Physique. L'invariance de L'espace Euclidien—316
Lind, S. C., The Chemical Effects of Alpha-Particles and Electrons—150
Lyon, Darwin O., Das Periodische System in Neuer Anordnung—999
Müller-Pouillet Lehrbuch der Physik, Band V, Part II, Physik des Kosmos, P. Ten Bruggencate, R. Emden, K. Graff, J. Hellerich, J. Hopmann, H. Kienle, E. von der Pahlen, C. Wirtz, A. Kopff—532
Peirce, Benjamin Osgood, Mathematical and Physical Papers, 1903–1913—317
Redfield, John, Music: A Science and an Art—151
Schroedinger, E., Abhandlungen zur Wellenmechanic—150
Seeliger, Rudolph, Physik der Gasentladungen —840
Semenoff, N., and Alexander Walther, Die Physikalischen Grundlagen der Elektrischen Festigkeitslehre—531
Stark, J., Atomstruktur und Atombindung—998

Chemical combination
Relation to structure of *K* absorption limit, B. Davis, H. Purks—336

Chemical reaction
In H_2, O_2 mixtures, effect of electric discharge, R. D. Rusk—287
Mass action law, integrated equations, J. A. Beattie—691
Mass action law, relation for pure gases, J. A. Beattie—699

Conductivity, electrical (see Electrical conductivity and resistance)

Cosmic rays
Origin, R. A. Millikan, G. H. Cameron—533

Crystals and crystal structure
Atomic structure-factor curves, theory, G. E. M. Jauncey, W. D. Claus—12
Of calcite, grating space, A. P. R. Wadlund—841
Of Fe in thin films, effect of magnetic field, T. D. Yensen—114
Of Bi, Sn, produced in magnetic field, electrical properties, A. Goetz—322(A)

Cybotactic state
In liquids, theory, G. W. Stewart—558
In organic liquids, G. W. Stewart—153

Dielectric constant (see also Refractive index)
Of air at radio frequencies, A. B. Bryan, I. C. Sanders—302
Of CO, COS, CS_2, H_2S, and electric moment, C. T. Zahn, J. B. Miles Jr.—497

Dielectrics
Anomalous dispersion, absorption and Kerr effect, effect of temperature and viscosity, D. W. Kitchin, H. Müller—979

Diffraction of radiation
Of x-rays in liquids, theory, G. W. Stewart, 558
Of x-rays in organic liquids, G. W. Stewart—153

Diffraction of sound
By a rigid sphere, theory, S. Ballantine—988

Diffusion, gaseous
Of metastable atoms in Hg vapor, J. H. Coulliette —636

Discharge of electricity in gases (see also Arc)
In A, afterglow, ionic concentrations and recombination, C. Kenty—624
Effect of cathode temperature on sputtering, L. R. Ingersoll, L. O. Sordahl—649
In H_2, O_2 mixtures, number of H_2O molecules formed as function of pressure, R. D. Rusk —287
Ionic oscillations, L. A. Pardue, J. S. Webb—946

Discharge of electricity in high vacua (see also Thermionic emission)
Electric fields near tungsten wires of small diameter, C. C. Lauritsen, S. S. Mackeown—326 (A)

Dispersion of radiation
Anomalous, in NaCl and KCl, in far ultra-violet, A.H. Pfund—39
Anomalous, in viscous dielectrics, effect of temperature and viscosity, D. W. Kitchin, H. Müller—979
In excited neon, constants, R. N. Jones—691
In metals, number of free and bound electrons, R. Ruedy—974

Electrical conductivity and resistance
Of alloys under pressure, C. W Ufford—505
Of Bi and Sn single crystals formed in magnetic field, A. Goetz—322(A)
Of Fe, Cu, Au, Ag, Zn, in magnetic field, H. M. Brown—508

Electrical conductivity and resistance—cont.
Of Fe wire, at radio frequencies, G. R. Wait, F. G. Brickwedde, E. L. Hall—967
Statistical fluctuation of charge in conductors, J. B. Johnson—97
Thermal agitation of electric charge, H. Nyquist —110

Electric fields
Near tungsten wires of small diameter, C. C. Lauritsen, S. S. Mackeown—326(A)

Electrolytes
Fluorescent, e.m.f. as function of illumination, H. W. Russell—667

Electrolytic Cells
Photoactive, e.m.f. as function of illumination, H. W. Russell—667

Electrons
Charge, calculation based on x-ray measurements, A. P. R. Wadlund—841

Electrons in gases (see also Arc; Discharge of electricity in gases; Potentials, critical)
In A, excitation of extreme ultra-violet spectrum, K. T. Compton, J. C. Boyce, H. N. Russell —179
Absorption coefficients, mean free path in Hg vapor, T. J. Jones—459
Ionization of CH_4, analysis of ions, T. R. Hogness, H. W. Kvalnes—942
Ionization of CO, analysis of ions, T. R. Hogness, R. W. Harkness—936
Ionization of I_2, analysis of ions, T. R. Hogness, R. W. Harkness—784
Quantum theory of impacts, J. R. Oppenheimer —361
Activation of N_2, C. Kenty, L. A. Turner—799

Electrons in metals (see also Thermionic emission of electrons)
Number of free and bound electrons, from dispersion, theory, R. Ruedy—974
Statistical fluctuation of charge in conductors, J. B. Johnson—97
Thermal agitation, e.m.f. due to, H. Nyquist —110

Electrons, photoelectric (see Photoelectric effect)

Electrons, secondary
From Cs covered plate by impact of Cs^+ ions, J. M. Hyatt—922
From Mo, by electron impact, J. M. Hyatt, H. A. Smith—929

Electronic states (see Energy states)

Electromotive force
Due to thermal agitation of charge in conductors, H. Nyquist—110

Energy states (see also Spectra)
In atomic hydrogen, non metastability of $2s$ level, V. Rojansky, J. H. VanVleck—327(A)
In diatomic molecules VII, $^2P \rightarrow {}^2S$ and $^2S \rightarrow {}^2P$ transitions, R. S. Mulliken—388, Correction —997
Of Hg^{++}, mean life for λ 4797 line, L. R. Maxwell —721
Of complex molecules, distribution, O. K. Rice —142
In molecules; II. correlation of molecular and atomic states, R. S. Mulliken—761
Transition probabilities in excited neon, R. N. Jones—681

Entropy (see Thermodynamics)

Erythema meter
Design, R. C. Burt—320(A)

Field currents (see Discharge of electricity in high vacua)

Fine structure of spectrum lines
Of $2^3P_{0,1,2} - 2^3S_1$ of Hg, E. H. Collins—753
Of x-radiation scattered from C, B. Davis, D. P. Mitchell—331

Fluids
Flow of viscous incompressible fluids, C. B. Millikan—323(A)

Fluorescence
Of electrolytes, e.m.f. as function of illumination, H. W. Russell—667
Of mixtures of Hg and Zn vapors, J. G. Winans —427
Used for ultra-violet photometry, Wm. T. Anderson, Jr., L. F. Bird—293

Friction
In metals, internal, R. H. Canfield—520

Geophysics
Diamagnetic layer of earth's atmosphere, relation to variation of terrestrial magnetism, R. Gunn —133
Electrostatic induction of sun's charge upon earth, F. Sanford—325(A)

Hall effect
In electrolytic iron, relation to induction, E. M. Pugh—321(A), 824

Hamiltonian function
Quantum mechanically correct form, B. Podolsky —812

Heats of linkage
Of C-H bonds, from absorption spectra, J. W. Ellis—324(A)

Hydrodynamics
Steady motion of viscous incompressible fluids, C. B. Millikan—323(A)

Hysteresis (see Magnetic properties)

Instruments (see Methods and instruments)

Intensities in spectra (see also Spectra, X-rays)
Of a.c. arc, variation, B. O'Brien, E. D. O'Brien 321(A)
In HCl bands, calculation, D. G. Bourgin—237
Of He, effect of pressure and current density, A. C. Hodges—319(A)
Of He, variation with potential near 54 volts, I. C. Cornog—746
Of He, variation with pressure and potential, C. Hodges, W. C. Michels—913
Of Hg, L. R. Maxwell—715
Of Hg arc, E. O. Hulburt—593
In *L*-spectrum of U, S. K. Allison—1

Interference of light
After reflection, explanation of absence of thermokinetic effect, P. S. Epstein—328(A)

Ionization in gases (see also Electrons in gases; Potentials, critical)
By electrons in CO, analysis of ions, T. R. Hogness, R. W. Harkness—936
By electrons in CH_4, analysis of ions, T. R. Hogness, H. W. Kvalnes—942
By electrons in I_2, analysis of ions, T. R. Hogness, R. W. Harkness—784
By K^+ ion impact in H_2 at 7000 volts, efficiency, R. W. Gurney—795
By x-rays, method of measurement with ballistic electrometer, D. L. Webster, R. M. Yeatman —327(A)
By collisions of second kind, analysis of ions, H. D. Smyth, E. C. G. Stueckelberg—779

Ions (see also Ionization in gases; Ions, mobility)
Nature of, from mobilities, L. B. Loeb—81
Oscillations in glow discharge, L. A. Pardue, J. S. Webb—946
Recombination in x-ray spectrometer, D. L. Webster, R. M. Yeatman—325(A)
Concentration in argon afterglow, C. Kenty—624

Ions (see also Ionization in gases; Ions, mobility)—cont.
Of Cs, secondary electron emission from, J. M. Hyatt—922

Scattering from Pt surface, velocity and angle distribution, critical energy, R. W. Gurney —467

Ions, mobility
Effect of water vapor, H. A. Erikson—791
Relation to nature of ions, L. B. Loeb—81

Isotopes
Of Ne, existence of Ne_{11}, T. R. Hogness, H. W. Kvalnes—942

Kerr effect
In viscous dielectrics, effect of temperature and viscosity, D. W. Kitchin, H. Müller—979

Magnetism
Ultimate nature of, T. D. Yensen—114

Magnetic properties
Of Fe films, as affecting crystal structure, T. D. Yensen—114
Anomalous magnetic rotation in excited neon, R. W. Jones—681
Heat emission in magnetic hysteresis, F. W. Constant—486
Effect of electrical properties of forming single crystals of Bi and Sn in magnetic field, A. Goetz—322(A)
Effect of field on thermal and electrical conductivity of Fe, Cu, Au, Ag, Zn, H. M. Brown —508
Hall effect and magnetic induction in electrolytic iron, E. M. Pugh—321(A), 824
Coercive force of Ni evaporated films, K. J. Miller—689
Paramagnetism of Fe salts, negative values of θ, L. A. Welo—320(A)
Permeability of Fe wire at radio frequencies, G. R. Wait, F. G. Brickwedde, E. L. Hall—967
Of permalloy, time-lag, R. M. Bozorth—124
Susceptibilities of HCl and NO, absence of effect of electric field, L. M. Mott-Smith—817

Mass action law
For chemical reactions, integrated equations, J. A. Beattie—691
For chemical reaction, relations for pure gases, J. A. Beattie—699

Mechanics, quantum
Correct form of Hamiltonian function, B. Podolsky—812
Lagrangian functions which determine a symmetrical tensor by Schroedinger's rule, H. C. Hicks—322(A)
Measurable functions of dynamical variables, B. Cassen—326(A)
Non-metastability of 2*s* level of atomic hydrogen, V. Rojansky, J. H. VanVleck—327(A)
Of normal state of He, J. C. Slater—349
Nuclear motions associated with electron transitions in diatomic molecules, E. U. Condon —858
Polarization of resonance radiation, F. C. Hoyt —377
Principle of uncertainty in Weyl's system, G. Breit—570
Propagation of Schroedinger waves in a uniform field of force, G. Breit—273
Of rotational distortion of multiplets in molecular spectra, E. Hill, J. H. VanVleck—250
Self consistent field and atomic structure, J. C. Slater—339
Of σ-type doublets in molecular spectra, J. H. VanVleck, R. S. Mulliken—327(A)
Theory of electron impacts, J. R. Oppenheimer —361

Mechanics, statistical
Generalized Gibbs-Boltzmann equation, F. R. Bichowsky—494

Metastable state (see also Activated gases)
Of Hg, diffusion of atoms, photoelectric action, J. H. Coulliette—636

Methods and instruments
For determining critical potentials in metallic vapors, H. B. Wahlin—277
For determining specific heats, T. E. Stern—298
For measuring arc voltage across opening switch contacts, H. Hamilton—322(A)
For measuring ultra-violet quanta, W. T. Anderson, Jr., L. F. Bird—293
Double x-ray spectrometer, theory, M. M. Schwarzschild—162
Erythema meter, R. C. Burt—320(A)
Optical oscillograph, S. Smith—319(A)
Photoelectric control with mirror reading instruments, K. Lark-Horovitz, G. W. Sherman —328(A)
Quartz oscillators, temperature coefficient, R. S. Strout—829
Vacuum switch, contact behavior, F. C. Lindvall —321(A)

Methods and instruments—cont.
X-ray tube for 1500 kv, C. C. Lauritsen, R. D. Bennet—322(A), 850
X-ray dosage measurements by ionization as affected by recombination, D. L. Webster, R. M. Yeatman—325(A)
For insulation from vibration, V. O. Knudsen —324(A)
Photometer, ultra-violet, R. C. Burt—326(A)
For ionization measurements ballistic use of electrometer, D. L. Webster, R. M. Yeatman —327(A)
Cathode sputtering, effect of temperature, L. R. Ingersoll, L. O. Sordahl—649
Precision method for near infra-red spectroscopy, J. Barnes, W. H. Fulweiler—618

Mobility (see Ions, mobility)

Molecular structure
Of CO, COS, CS_2, H_2S, electric moment, C. T. Zahn, J. B. Miles, Jr.—497
Assignment of quantum numbers I, R. S. Mulliken —186
Assignment of quantum numbers II, R. S. Mulliken—761
Electronic states in diatomic gases, R. S. Mulliken —388, Correction—997
Of carbonates, from spectra, H. H. Nielsen—773
Of benzene, from spectra, J. Barnes, W. H. Fulweiler—618
Of methyl halides, from spectra, W. H. Bennett, C. F. Meyer—888

Optics, geometrical
Locus of secondary image for two plane mirrors, L. E. Dodd—320(A)

Oscillograph
Optical, S. Smith—319(A)

Oscillators, quartz
Temperature coefficient, R. S. Strout—829

Penetrating radiation (see Cosmic rays)

Photoelectric effect
Of clean Hg, long wave-length limit, effect of gases, W. B. Hales—950
Direction of ejection of electrons, H. E. Ives, A. R. Olpin, A. L. Johnsrud—57
Fatigue and thresholds for Ca, Fe, Co, Ni, Cu, Zn, and Ge, G. B. Welch—657
For Hg, effect of toluene vapor, D. Roller—323 (A)
Of polarized x-rays, direction of ejection of photoelectrons, C. J. Pietenpol—564

Photoelectric Effect—cont.
From Pt and Pd, work function and temperature, L. A. DuBridge—325(A)
Time of appearance and cessation, E. O. Lawrence J. W. Beams—478
Voltage-current relations in central cathode cells, T. C. Fry, H. E. Ives—44
Of W, variation with temperature and long wave-limit, A. H. Warner—326(A)
Of x-rays, direction of ejection of electrons, J. A. Van den Akker, E. C. Watson—323(A)
Used as control in mirror reading instruments, K. Lark-Horovitz, G. W. Sherman—328(A)

Photometer
For ultra-violet, R. C. Burt—326(A)

Photometry
In ultra-violet, by fluorescence, Wm. T. Anderson, Jr., and L. F. Bird—293

Polarization of light
Of resonance radiation, H. F. Olson—443
Of resonance radiation, quantum theory, F. C. Hoyt—377

Potentials, critical
For electrons in A, for extreme ultra-violet spectrum, K. T. Compton, J. C. Boyce, H. N. Russell—179
For electrons in CO, T. R. Hogness, R. W. Harkness—936
For electrons in CH_4, T. R. Hogness, H. W. Kvalnes—942
For electrons in I_2, T. R. Hogness, R. W. Harkness—784
For electrons in Cu vapor, H. B. Wahlin—277
For electrons in Hg vapor, comparison of measurements, J. C. Morris—447
For ionization of methane, ethane, ethylene, and acetylene, J. C. Morris—456
Of light atoms, ionization from spectra, L. A. Turner—727

Quantum theory (see Mechanics, quantum)

Radiation, thermal
From incandescent oxides, characteristics, M. L. Phillips—832

Radio (see Wireless)

Recombination of ions (see also Spectra, recombination)
Rate, in argon afterglow, C. Kenty—624

Reflection of light
Metallic, from NaCl and KCl in far ultra-violet, A. H. Pfund—39

Refractive index
Of Na vapor, relation to *D* line-width, J. Q. Stewart, S. A. Korff—676

Residual ionization (see Cosmic rays)

Resistance, electrical (see Electrical conducivity and resistance)

Resonance radiation
Polarization, H. F. Olson—443
Polarization, quantum theory, F. C. Hoyt—377

Space charge
Concentration near insulating surface, B. Cassen—323(A)

Specific heat
Of Mo, T. E. Stern—298
Relation to thermal conductivity and temperature, C. C. Bidwell—311

Spectra, atomic
Of A, extreme ultra-violet, critical potentials, analysis, K. T. Compton, J. C. Boyce, H. N. Russell—179
Of A, in afterglow, recombination, C. Kenty—624
Of H, non-metastability of $2s$ level, theory, V. Rojansky, J. H. VanVleck—327(A)
Of Hg arc, intensities of lines, E. O. Hulbert—593
Of He, in arc, Doppler broadening, J. M. Dewey—918
Of As II, wave-lengths and classification, C. W. Gartlein—320(A)
Of As IV, AsV, Se V, Se VI, analysis, R. A. Sawyer, C. J. Humphreys—583
Of Ag III, analysis, R. C. Gibbs, H. E. White—318(A)
Of As III, Sb III, Bi III, wave-length and cassification, R. J. Lang—737
Of He, variation with pressure and potential of intensities of lines, C. Hodges, W. C. Michels—913
Of He, variation of intensity with potential, I. C. Cornog—746
Of He, effect of pressure and current density, A. C. Hodges—319(A)
Of Hg, above ionizing potential, L. R. Maxwell—715
Of Hg, fine structure of $2^3P_{0,1,2}-2^3S_1$, E. H. Collins—753
Of Hg^{++}, mean life for $\lambda 4797$, L. R. Maxwell—721
Of light atoms, critical potentials, L. A. Turner—727

Spectra, atomic—cont.
Of Na and Mg, variation of intensity in a.c. arc, B. O'Brien, E. D. O'Brien—321(A)
Of Ne, spark spectra, wave-lengths, A. S. Ganesan —580
Of Pd II, classification, A. G. Shenstone—30
Of Pr, structure of lines, A. S. King—319(A)
Solar, examination of Langley's bolometric data H. D. Babcock—326(A)
Of Sb IV, extension of iso-electronic sequence, A. M. Vieweg, R. C. Gibbs—320(A)
Of S II, wave-lengths and classification, S. B. Ingram—172, 318(A)
Of V III, Cr IV, analysis, H. E. White—318(A)
Of Zn and Hg, fluorescence and absorption of HgZn mixtures, J. G. Winans—427

Spectra, molecular
Assignment of quantum numbers I, R. S. Mulliken —186
Assignment of quantum numbers II, R. S. Mulliken—761
Of BeH, analysis, W. W. Watson—600
Of organic liquids, absorption, J. W. Ellis—324 (A)
Of carbonates, vibration spectra, theory, H. H. Nielsen—773
Of CO and NO, excited by active nitrogen, H. P. Knauss—417
Of HgTl and InCd, bands, R. K. Waring—435
Of Hg_2, Zn_2, HgZn in fluorescence and absorption, J. G. Winans—427
Of ICl, wave-lengths and classification, E. D. Wilson—611
Of liquid benzene, infra-red, nature of absorber, J. Barnes, W. H. Fulweiler—618
Of methyl halides, infra-red absorption, wave-lengths and analysis, W. H. Bennett, C. F. Meyer—888
Of HCl, intensities, theory, D. G. Bourgin—237
Of Na_2, rotational structure of blue-green bands, F. W. Loomis, R. W. Wood—223
Of Na_2, red system of bands, new features, F. W. Loomis, S. W. Nile Jr.—873
Of O_2 atmospheric absorption, interpretation, R. S. Mulliken—880
In organic liquids, absorption, J. W. Ellis—906
Rotational distortion of multiplets in molecular spectra, E. Hill, J. H. VanVleck—250
Width of σ-type doublets, theory, J. H. VanVleck, R. S. Mulliken—327(A)
Of SnCl, classification, W. F. C. Ferguson—607
Structure in diatomic molecules, R. S. Mulliken — 388, Correction— 997
Theory of nuclear motions associated with electron transitions in diatomic molecules, E. U. Condon—858

Spectra, recombination
In argon afterglow, C. Kenty—624
In electric arc, J. M. Dewey—918

Spectra, solar
Extension to the photographic study, H. D. Babcock, W. P. Hoge—327(A)
Examination of Langley's bolometric data, H. D. Babcock—326(A)

Sputtering
Effect of cathode temperature, L. R. Ingersoll, L. O. Sordahl—649

Statistical mechanics (see Mechanics, statistical)

Structure-factor curves
In crystal reflection of x-rays, G. E. M. Jauncey, W. D. Claus—12

Surface layers (see Adsorption)

Terrestrial magnetism and electricity (see Geophysics)

Thermal capacity (see specific heat)

Thermal conductivity
Of Fe, Cu, Au, Ag, Zn, in magnetic field, H. M. Brown—508
Relation to specific heat and temperature, C. C. Bidwell—311

Thermionic emission
From Pt and Pd, work function and temperature, L. A. DuBridge—325(A)
From Pt, values of constants of pure metal, L. A. DuBridge—961
Surface heat of charging, L. Tonks—284

Thermodynamics
Entropy and thermodynamic potentials of real gases and mixtures, II. Integrated equations, J. A. Beattie—691
Entropy and thermodynamic potentials for real gases and mixtures, II. Relations for pure gases and equilibrium pressure of gas in a mixture, J. A. Beattie—699
Equilibrium between radiation and matter, F. Zwicky— 324(A)
Generalized Gibbs-Boltzmann equation, F. R. Bichowsky—494

Thermoelectric effect
Between single crystals of Sn or Bi formed in and outside a magnetic field, A. Goetz—322(A)

The rmoluminescence
Of glass, R. E. Nyswander, B. E. Cohn— 321(A)

Ultrasonic waves (see Acoustics)

Uncertainty principle (see Mechanics, quantum)

Vacuum switch
Contact behavior and gas phenomena, F. C. Lindvall—321(A)

Vibration
Method of insulating from, V. O. Knudsen—324 (A)

Viscosity
Flow of viscous, incompressible fluids, C. B. Millikan—323(A)
In dielectrics, effect on dispersion, absorption, Kerr effect, D. W. Kitchin, H. Müller—979

Wave mechanics (see Mechanics, quantum)

Wireless
Temperature coefficient of quartz oscillators, R. S. Strout—829

Work function (see Discharge of electricity in high vacua; Photoelectric effect, Thermionic emission of electrons)

X-rays, absorption
Effect of chemical combination and temperature on *K* limits, B. Davis, H. Purks—336

X-rays, crystal analysis (see Crystals)

X-rays, diffraction
In organic liquids, G. W. Stewart—153
In liquids, theory, G. W. Stewart—558

X-rays, general
Superposition of x-ray beams, absence of Barkla effect, G. L. Pearson, Wm. H. Hansen—325(A)

X-rays, photoeffect
Direction of ejected electrons, J. A. Van den Akker, E. C. Watson—323(A)
Direction of ejected electrons, C. J. Pietenpol —564

X-rays, reflection
From crystals, structure-factor curves, theory, G. E. M. Jauncey, W. D. Claus—12
Total, from Ni films, H. W. Edwards— 712

X-rays, scattering
By C, fine structure, B. Davis, D. P. Mitchell —331
By gases, C. S. Barrett— 22

X-rays, spectra
Relative intensities in *L*-spectrum of U, S. K. Allison—1
Absolute wave-length measurements of Kα, of Cu, Fe, Mo, A. P. R. Wadlund—841
Wave-length of C Kα, B. B. Weatherby—707

X-ray, technique and instruments
High voltage tube for 1500 kv, C. C. Lauritsen, R. D. Bennett—322(A), 850
Double x-ray spectrometer, theory, M. M. Schwarzschild—162

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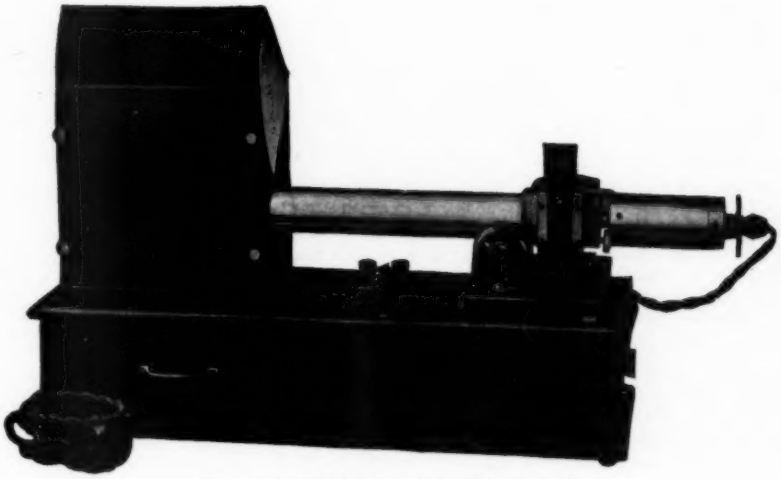

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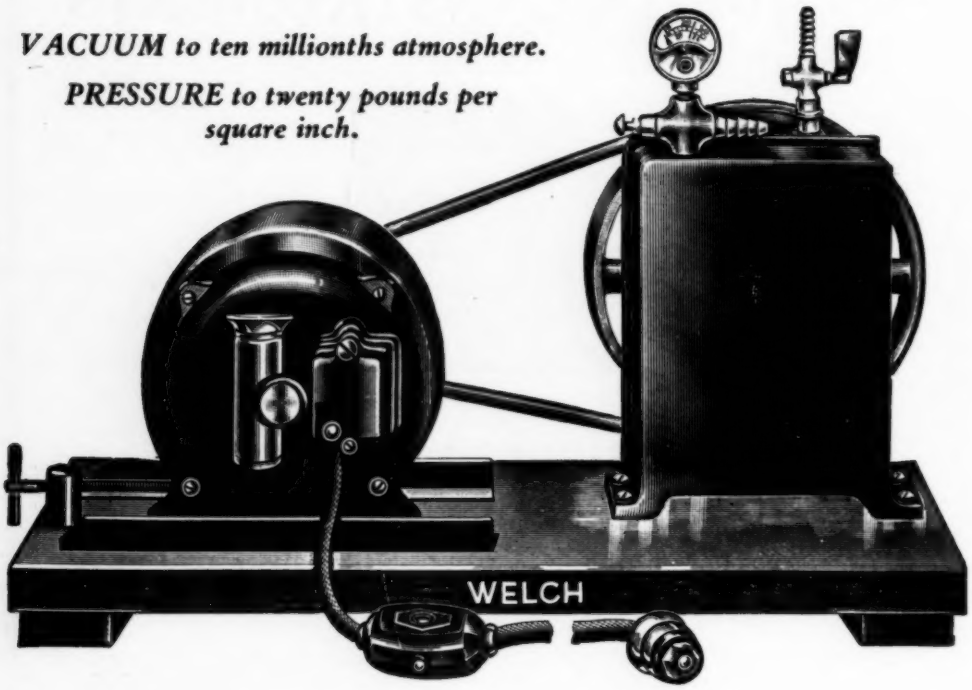

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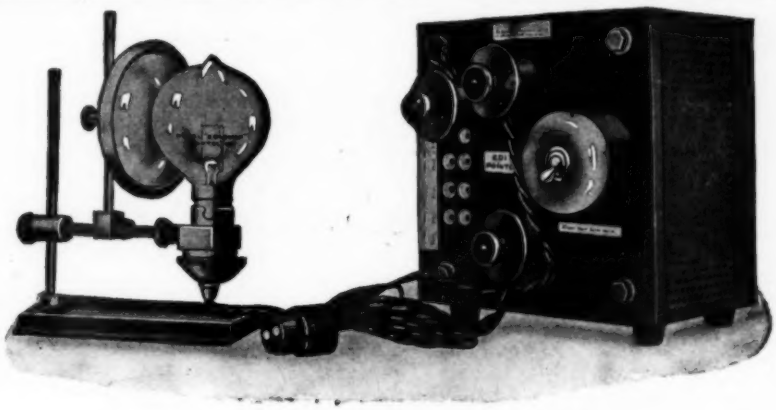

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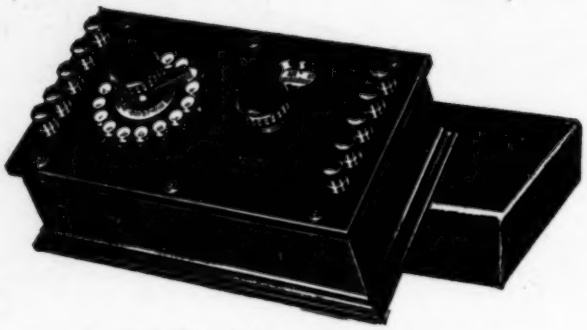

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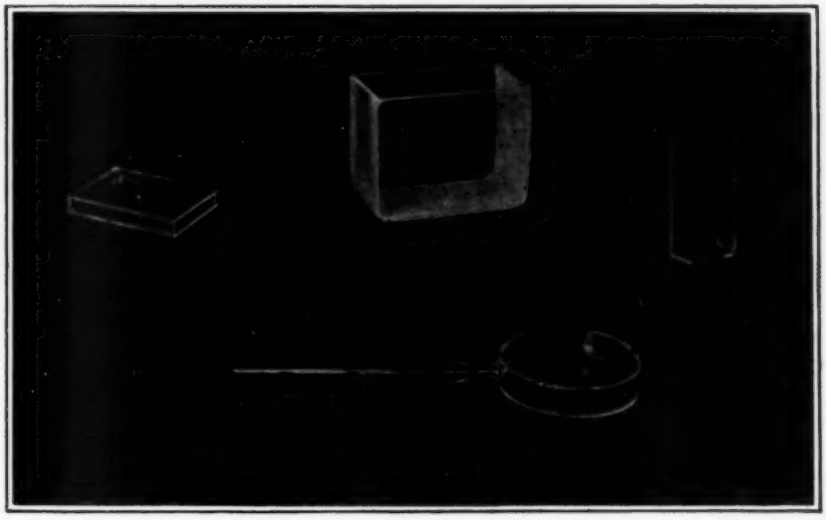

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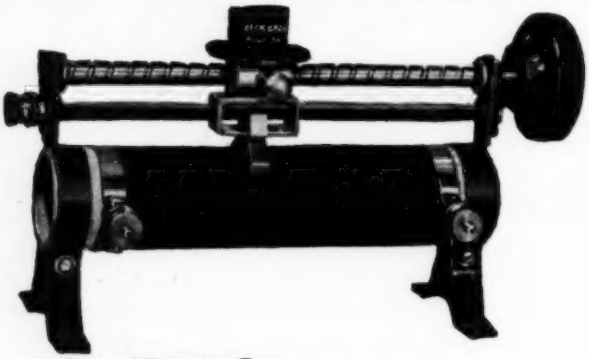

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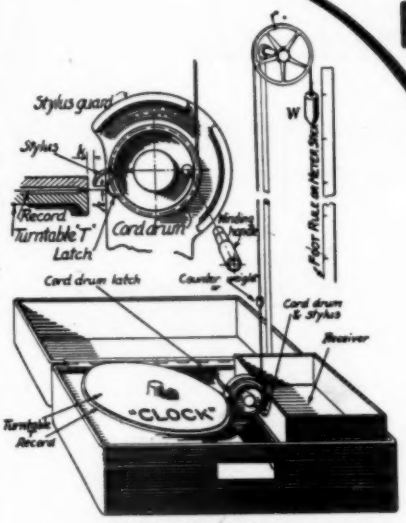

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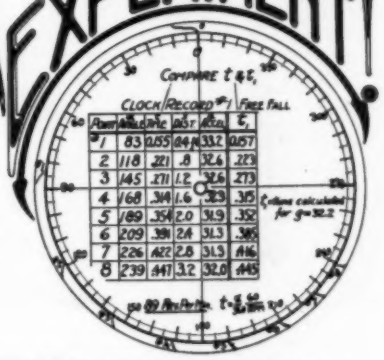

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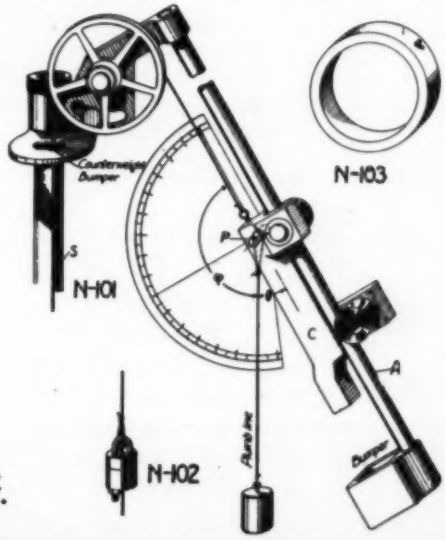

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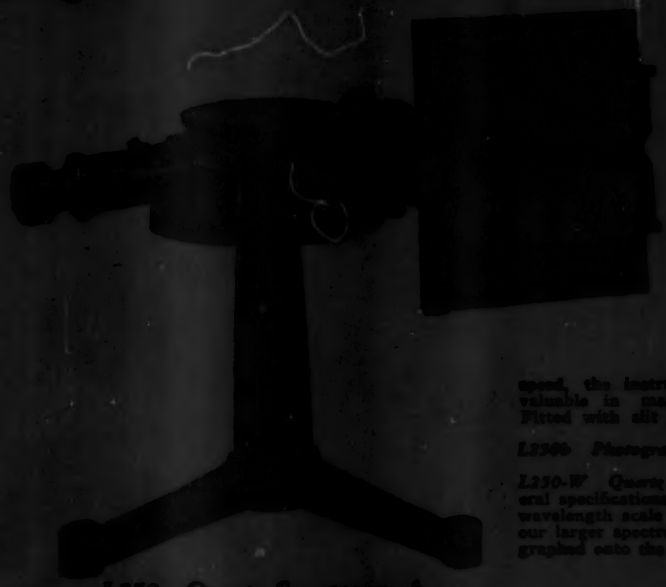

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